

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
31 October 2002 (31.10.2002)

PCT

(10) International Publication Number  
WO 02/085988 A1

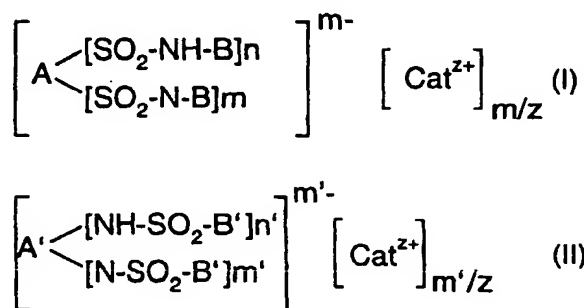
- (51) International Patent Classification<sup>7</sup>: C09B 69/02, 69/00, 67/44, 67/00, C09D 11/00
- (21) International Application Number: PCT/EP02/04071
- (22) International Filing Date: 11 April 2002 (11.04.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
01810383.8 19 April 2001 (19.04.2001) EP
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- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
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Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: WATER-SOLUBLE SALT OF SULFONAMIDES AS COLORANTS FOR THE PIGMENTING OF POROUS MATERIALS AND FOR USE IN INKJET PRINTING



(57) Abstract: The present invention relates to colorants of the general formula, wherein A, B and B', m and m' and n and n' are as defined in the description. The colorants can be used for the pigmenting of porous materials and in inkjet printing and, in the case of pigmenting, are converted to the insoluble pigment form. In the pigmenting of porous materials, for example in the pigmenting of wood or anodised aluminium in the pores, the colorants yield very good penetration and fastness to light and, in inkjet printing, yield very good water-resistance.

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Water-soluble salts of sulfonamides as colorants for the pigmenting of porous materials and for use in inkjet printing

- 5 The present invention relates to water-soluble salts of sulfonamides that can be used as colorants for the pigmenting of porous materials and in inkjet printing and, in the case of pigmenting, are converted to the insoluble pigment form. In the pigmenting of porous materials, for example in the pigmenting of wood or anodised aluminium in the pores, the water-soluble salts of sulfonamides yield very good penetration and fastness to light and, in inkjet printing, yield very good water-resistance.

10 DE-A-2757226 describes a method of dyeing fibre materials consisting wholly or partially of cellulose, wherein a mono- or dis-azo dye having a sulfonamide group is applied to the fibre material in an alkaline aqueous solution and is fixed to the fibre material by means of subsequent acid treatment in the acid pH range. The dyeings exhibit good in-use fastness properties, especially fastness to washing.

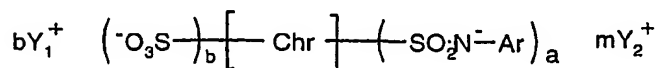
15 Water-soluble phthalocyanine dyes are described in EP-A-0 024 677. They are substituted by at least one  $-\text{SO}_2\text{-NH-CN}$  group and may contain an  $-\text{SO}_2\text{-NY}^1\text{Y}^2$  group wherein  $\text{Y}^1$  and  $\text{Y}^2$  denote a hydrogen atom or an unsubstituted or substituted alkyl group. The phthalocyanine dyes are suitable as water-soluble dyes for the dyeing and printing of fibre materials, it being preferred to use them in the form of their ammonium salts. They are generally applied in a neutral or acidic aqueous medium and are fixed to the material by means of moderate or high temperature.

20 US-A-3 972 904 relates to water-soluble sodium or ammonium salts of the following formula



wherein F is the radical of a water-insoluble dye, A is  $-\text{O}-$ ,  $-\text{S}-$ ,  $-\text{NY}^3-$  ( $\text{Y}^3 = \text{H}$ , alkyl, etc.) and Me is an alkali metal atom or an ammonium ion. The water-insoluble dyes must contain an  $\text{OH-}$ ,  $\text{SH-}$  or  $\text{NHY}^3$  group. The salts are used for dyeing polyester. The regeneration of the water-soluble dye is achieved by heating.

30 DE-A-197 11 445 relates to dye salts of formula



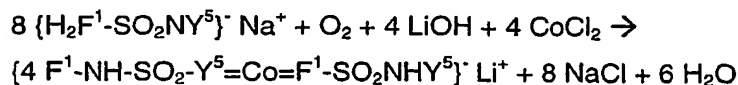
, wherein Chr is an  $(m + n)$ -valent radical of a chromophore from the series of phthalocyanines that are metal-free or contain metal, quinacridones, mono-, dis- or poly-azo dyes, anthraquinones or copper formazanes, Ar is unsubstituted or substituted phenyl or unsubstituted or substituted

naphthyl,  $Y_1^+$  is a metal cation or ammonium ion,  $Y_2^+$  is a proton, a metal cation or ammonium ion, a is from 1 to 6 and b is from 1 to 6, the sum of a and b being a maximum of 6, and to the use of the dye salts in the dyeing of polymeric material.

DE-A-199 58 181 discloses diketopyrrolopyrrole-based pigment dispersants that contain sulfonamide groups in addition to sulfonic acid groups.

GB-1 198 501 relates to a method of dyeing polyester using dyes of the formula phthalocyanine-(Y-Y<sup>4</sup>)<sub>n</sub> wherein Y can be an -SO<sub>2</sub>NH-, CH<sub>2</sub>SO<sub>2</sub>-NH-phenylene-O- or CH<sub>2</sub>SO<sub>2</sub>NH-phenylene-C(O)O- group and Y<sup>4</sup> denotes a lower alkyl or acyloxy-lower alkyl group (see Examples 10, 11 and 21).

- 10 US-A-4 000 965 discloses that stable solutions of 1:2 chromium or 1:2 cobalt complexes of monoazo, disazo or polyazo dyes or azomethine dyes can be obtained in organic solvents that contain hydroxy groups, or in mixtures thereof with water in the presence of alkaline lithium salts. There are described sodium salts of metal-free intermediates of metal complex dyes that carry an -SO<sub>2</sub>NY<sup>5</sup>Na group, wherein Y<sup>5</sup> can be a hydrogen
- 15 atom or an alkyl, aryl or acyl radical, and that are converted to the metal complex dyes in accordance with the following equation:



- wherein Y<sup>5</sup> is as defined above and F<sup>1</sup> is the radical of one of the above-mentioned dyes (see also US-A-3 617 176).

- 20 DE-A-2545393 describes dye salts, free of complex-bound metal, having an SO<sub>3</sub>Met group or an SO<sub>2</sub>-NMet-SO<sub>2</sub> group, wherein Met is an alkali metal, and at least one further acid group, at least 20% of which has been converted to the alkali salt, which acid group forms alkali salts only at a pH greater than 8.
- 25 Suitable acid groups that form alkali salts only at a pH > 8 are phenolic and enolic OH groups and, advantageously, sulfonic acid amide groups of formula -SO<sub>2</sub>NH-Y<sup>6</sup>, wherein Y<sup>6</sup> is hydrogen, unsubstituted or substituted C<sub>1-4</sub>alkyl, aryl or aralkyl. The dye salts are very readily soluble in both hot water and cold water.

- Numerous pigments modified with sulfonamide groups have been described. The conversion of the sulfonamide groups to the salt form and the use of pigments modified in such a manner for the pigmenting of porous materials and in inkjet printing, however, have not yet been described.

- 30 WO-98/58027 (porous materials in general), WO00/36210 (wood), EP00/09376 (wood), EP-A-1044945 (pencil leads), WO00/17275 (colour filters) and WO00/27930 (metal

oxides) relate to the pigmenting of porous materials, starting from soluble pigment precursors.

The problem of the present invention is accordingly to provide water-soluble colorants that can be converted readily to the insoluble pigment form and, in the pigmenting of porous materials, for example wood, yield very good penetration and very good fastness to light and, in inkjet printing, yield very good water-resistance.

Surprisingly, it has now been found that the problem is solved by using salts of primary or secondary sulfonamide groups as solubilising groups.

The present invention accordingly relates to colorants of the general formula



wherein n and n' denote a value from 0 to 4,

m and m' denote a value from 1 to 8, the sum of m + n and of m' and n' being less than or equal to 8,

z is an integer from 1 to 5, especially 1,

A is the radical of a chromophore of the series 1-aminoanthraquinone, anthraquinone, anthrapyrimidine, azo, azomethine, benzodifuranone, quinacridone, quinacridone-quinone, quinophthalone, diketopyrrolopyrrole, dioxazine, flavanthrone, indanthrone, indigo, isoindoline, isoindolinone, isoviolanthrone, perinone, perylene, phthalocyanine; pyranthrone or thioindigo,

A' is the radical of a chromophore that already contains one or more primary amino groups, such as 1-aminoanthraquinone, or A' is one of the chromophore radicals listed under A modified with from 1 to 8, preferably with from 1 to 4, amino groups,

Cat is an alkali metal cation or an ammonium cation and

B and B' are each independently of the other a branched or straight-chain C<sub>1-8</sub>alkyl, C<sub>2-8</sub>alkenyl, C<sub>2-8</sub>alkynyl, aryl, N-, O- or S-containing 5- or 6-membered heterocyclic ring, C<sub>1-8</sub>alkylarylene, aryl-C<sub>1-8</sub>alkylene or aryl-L-arylene radical, which may be substituted by one or more groups -OH, -OCat, -SH, -SCat, -OR<sup>1</sup>, -SR<sup>2</sup>, -C(O)OR<sup>3</sup>, -C(O)R<sup>4</sup> and/or -NR<sup>5</sup>R<sup>6</sup>, it being possible for the C<sub>1-8</sub>alkyl radical to be uninterrupted or interrupted one or more times by -O- or by -S-,

$R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are each independently of the others a  $C_{1-8}$ alkyl radical, a  $C_{7-11}$ aralkyl radical or a  $C_{6-10}$ aryl radical and  $R^4$  can additionally be a hydrogen atom,

L is a bond,  $-NR^7$ , wherein  $R^7$  is a hydrogen atom or a  $C_{1-4}$ alkyl radical, or an  $-N=N-$  group, and  $R^5$  and  $R^6$  are each independently of the other a hydrogen atom, a  $C_{1-8}$ alkyl radical, a  $C_{1-4}$ alkoxy- $C_{1-4}$ alkyl radical, a  $C_{6-10}$ aryl radical, a  $C_{7-11}$ aralkyl radical or a radical

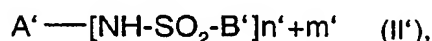
$-(CH_2)_oOH$ , wherein o is an integer from 2 to 6, and B can additionally be a hydrogen atom, it being possible for B and B' within a chromophore A or A' to have different substituent meanings.

The present invention relates also to the use of colorants of the general formulae I and II for the pigmenting of porous materials, especially for the pigmenting of wood or of anodised aluminium in the pores, and, in inkjet printing, to a method of pigmenting a porous material, especially for the pigmenting of wood or anodised aluminium in the pores,

comprising

a) treatment of the substrate with an aqueous solution of the colorant of general formula I or II and

b) conversion of the colorant to a pigment of formula I' or II', respectively,



wherein A and A', B and B', m and m' and n and n' are as defined above, and to porous materials that are obtainable by that method, and to porous materials that include pigments of general formula I' or II'.

Insoluble pigments that have a secondary or primary sulfonamide group can be rendered water-soluble in the form of a salt, especially in the form of the ammonium, sodium or potassium salt. The colorant is converted back to the water-insoluble pigment form by protonation, for example by the addition of acids.

Ligneous materials that have been pigmented using the colorants according to the invention, even in highly dilute concentrations, exhibit very good penetration and very good fastness to light. In the pigmenting of anodised aluminium good results are also obtained with the colorants according to the invention, that is to say especially homogeneous coloration and very good fastness to light. In inkjet printing, special mention

may be made in particular of the very good water-resistance of the colorants according to the invention.

In groups B and B', the radicals can have the following meanings:

5 alkyl or alkylene can be straight-chained or branched.

C<sub>1-8</sub>alkyl is, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethylpropyl, hexyl, heptyl, 2,4,4-trimethylpentyl, 2-ethylhexyl or octyl, which may be unsubstituted or substituted by -OH, -OCat, -SH, -SCat, -OR<sup>1</sup>, -SR<sup>2</sup>, -C(O)OR<sup>3</sup>, -C(O)R<sup>4</sup> or by -NR<sup>5</sup>R<sup>6</sup>, wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are as defined above.

10 Examples of C<sub>2-8</sub>alkenyl, which may also contain two double bonds which may be isolated or conjugated, are vinyl, allyl, 2-propen-2-yl, 2-buten-1-yl, 3-buten-1-yl, 1,3-butadien-2-yl, 2-penten-1-yl, 3-penten-2-yl, 2-methyl-1-buten-3-yl, 2-methyl-3-buten-2-yl, 3-methyl-2-buten-1-yl or 1,4-pentadien-3-yl, which may be unsubstituted or substituted by -OH, -OCat, -SH, -SCat, -OR<sup>1</sup>, -SR<sup>2</sup>, -C(O)OR<sup>3</sup>, -C(O)R<sup>4</sup> or by -NR<sup>5</sup>R<sup>6</sup>, wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are as defined above.

Preference is given especially to linear C<sub>1-5</sub>alkyl and C<sub>2-5</sub>alkenyl radicals terminally substituted by a group -OH, -OCat, -SH, -SCat, -OR<sup>1</sup>, -SR<sup>2</sup>, -C(O)OR<sup>3</sup>, -C(O)R<sup>4</sup> or -NR<sup>5</sup>R<sup>6</sup>. C<sub>2-8</sub>Alkyl that is interrupted one or more times by -O- or by -S- is, for example, interrupted 1, 2 or 3 times by -O- and/or by -S-, resulting, for example, in structural units such as -(CH<sub>2</sub>)<sub>2</sub>OCH<sub>3</sub>, -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, -CH<sub>2</sub>-O-CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>-O-CH<sub>2</sub>CH<sub>3</sub>, -[CH<sub>2</sub>CH<sub>2</sub>O]<sub>y</sub>-CH<sub>3</sub>, wherein y = 1-3, -CH<sub>2</sub>-CH(CH<sub>3</sub>)-O-CH<sub>2</sub>-CH<sub>2</sub>CH<sub>3</sub> or -CH<sub>2</sub>-CH(CH<sub>3</sub>)-O-CH<sub>2</sub>-CH<sub>3</sub>, which may be unsubstituted or substituted by -OH, -OCat, -SH, -SCat, -OR<sup>1</sup>, -SR<sup>2</sup>, -C(O)OR<sup>3</sup>, -C(O)R<sup>4</sup> or by -NR<sup>5</sup>R<sup>6</sup>.

25 Examples of C<sub>2-8</sub>alkynyl are ethynyl, 1-propyn-1-yl, 2-butyne-1-yl, 3-butyne-1-yl, 2-pentyn-1-yl and 3-pentyn-2-yl.

C<sub>1-8</sub>Alkylene is linear or branched alkylene, such as, for example, methylene, ethylene, propylene, isopropylene, n-butylene, sec-butylene, isobutylene, tert-butylene, pentylene, hexylene, heptylene, -CH(CH<sub>3</sub>)-CH<sub>2</sub>-, -CH(CH<sub>3</sub>)-(CH<sub>2</sub>)<sub>2</sub>-, -CH(CH<sub>3</sub>)-(CH<sub>2</sub>)<sub>3</sub>-,

30 -C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>- or 
$$\begin{array}{c} \text{CH}_3 \\ | \\ -\text{CH}_2-\text{C}-\text{CH}_2- \\ | \\ \text{C}_2\text{H}_5 \end{array}$$
, wherein alkylene radicals having from 1 to 5 carbon

atoms are preferred.

An alkylene radical interrupted by -O- or by -S- results, for example, in structural units such as -CH<sub>2</sub>-O-CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-O-CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>-CH(CH<sub>3</sub>)-O-CH<sub>2</sub>-CH(CH<sub>3</sub>)-,

$-\text{CH}_2-\text{S}-\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2-$  or  $-\text{CH}_2\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2\text{CH}_2-$ .

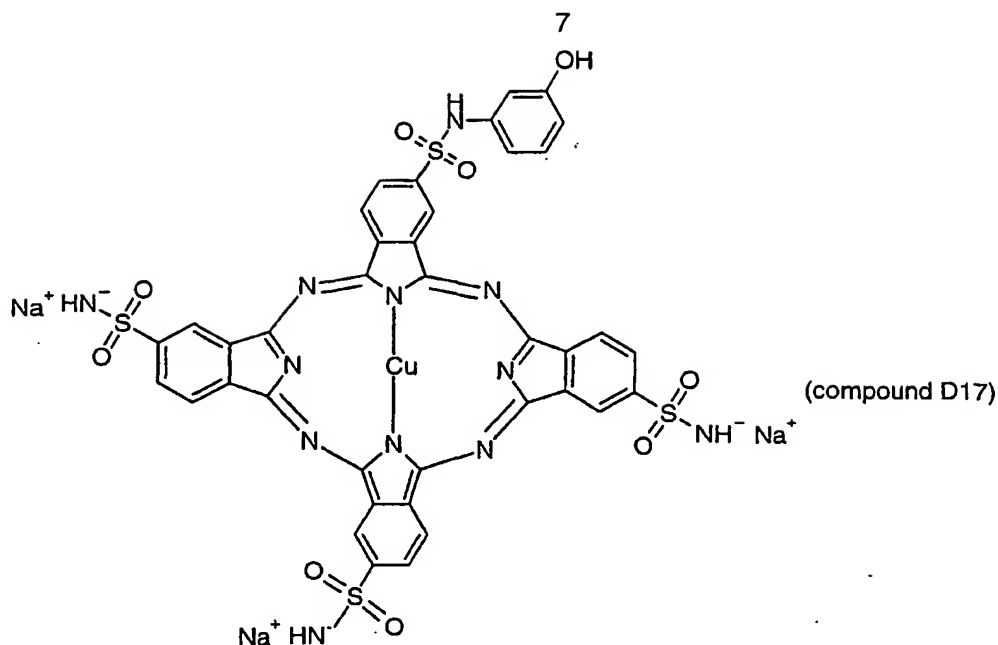
Examples of a  $\text{C}_{1-8}$ alkoxy radical, which may be linear or branched, are methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, isobutoxy, tert-butoxy, n-pentyloxy, 2-pentyloxy, 3-pentyloxy, 2,2-dimethylpropoxy, n-hexyloxy, n-heptyloxy, n-octyloxy, 1,1,3,3-tetramethylbutoxy and 2-ethylhexyloxy. According to the present invention, aryl is understood to mean especially an aryl radical having from 6 to 12 carbon atoms, examples thereof being phenyl, naphthyl and biphenyl, which may be substituted one, two or three times by linear or branched  $\text{C}_{1-4}$ alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl, by linear or branched  $\text{C}_{1-4}$ alkoxy, such as methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy or tert-butoxy, by linear or branched  $\text{C}_{1-4}$ alkylthio, such as methylthio, ethylthio, n-propylthio, isopropylthio, n-butylthio, isobutylthio, sec-butylthio or tert-butylthio,  $-\text{OH}$ ,  $-\text{SH}$ ,  $-\text{OCat}$ ,  $-\text{SCat}$  or by a group  $(\text{CH}_2)_e\text{-E}$ , wherein e is an integer from 1 to 6, especially 2 or 3, and E is a hydrogen atom, a group  $-\text{OH}$ ,  $-\text{OCat}$ ,  $-\text{SH}$ ,  $-\text{SCat}$ ,  $-\text{OR}^1$ ,  $-\text{SR}^2$ ,  $-\text{C}(\text{O})\text{OR}^3$ ,  $-\text{C}(\text{O})\text{R}^4$  or  $-\text{NR}^5\text{R}^6$ , wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are each independently of the others a  $\text{C}_{1-4}$ alkyl radical, especially methyl or ethyl, and  $\text{R}^5$  and  $\text{R}^6$  are a radical  $-(\text{CH}_2)_o\text{OH}$ , wherein o is an integer from 2 to 6, especially 2 or 3, and Cat is an alkali metal cation, especially a sodium or potassium cation, unsubstituted ammonium or an ammonium cation.

Preference is given to phenyl groups which may be substituted by one, two or three groups selected from  $-\text{OH}$ , methoxy,  $(\text{CH}_2)_2\text{OH}$ ,  $-\text{OCat}$  and  $(\text{CH}_2)_2\text{OCat}$ , such as, for example, 3,4,5-trimethoxyphenyl, 4-hydroxyphenyl, 3-hydroxy-4-methoxyphenyl and 2-hydroxy-1-ethylphenyl.

Examples of a  $\text{C}_{7-11}$ aralkyl radical which may be unsubstituted or substituted are benzyl, 2-benzyl-2-propyl,  $\beta$ -phenyl-ethyl,  $\alpha,\alpha$ -dimethylbenzyl and  $\omega$ -phenyl-butyl.

An O-, S- or N-containing 5- or 6-membered heterocyclic ring is, for example, pyrrolyl, oxinyl, dioxinyl, 2-thienyl, 2-furyl, 1-pyrazolyl, 2-pyridyl, 2-thiazolyl, 2-oxazolyl, 2-imidazolyl, isothiazolyl, triazolyl or any other ring system consisting of thiophene, furan, pyridine, thiazole, oxazole, imidazole, isothiazole, thiadiazole, triazole, pyridine and benzene rings that is unsubstituted or substituted by from 1 to 6 ethyl, methyl, ethylene and/or methylene substituents.

B and B' within a chromophore A or A' can have different substituent meanings, that is to say, according to the invention, for example, a copper phthalocyanine of the following formula is also included:



Suitable as anion Cat in the formulae (I) and (II) – and also in the groups -OCat and -SCat – are generally radicals that can form water-soluble salts with the sulfonamides. These are, for example, alkaline earth metal cations, such as strontium or calcium cations, alkali metal cations, especially lithium, sodium and potassium cations, and quaternary ammonium cations, especially unsubstituted ammonium and ammonium cations of the formula  $^+NR^{31}R^{32}R^{33}R^{34}$ , wherein  $R^{31}$ ,  $R^{32}$ ,  $R^{33}$  and  $R^{34}$  are each independently of the others a hydrogen atom, a straight-chain or branched  $C_{1-16}$ alkyl radical, which may be unsubstituted or substituted by one or more  $C_{1-4}$ alkoxy radicals, a straight-chain or branched  $C_{2-16}$ alkenyl radical, a hydroxy- $C_{1-8}$ alkyl radical, especially a hydroxy- $C_{1-4}$ alkyl radical, or a  $C_{6-12}$ aryl radical unsubstituted or substituted by one or more  $C_{1-4}$ alkyl radicals,  $C_{1-4}$ alkoxy radicals or hydroxy groups, especially a phenyl group substituted by a hydroxy group, or a  $C_{7-11}$ aralkyl radical, such as phenyl- $C_{1-4}$ alkyl, wherein at least one of the radicals  $R^{31}$ ,  $R^{32}$ ,  $R^{33}$  and  $R^{34}$  is other than a hydrogen atom, or two of the radicals  $R^{31}$ ,  $R^{32}$ ,  $R^{33}$  and  $R^{34}$  together with the nitrogen atom to which they are bonded form a 5- or 6-membered ring, which may contain additional hetero atoms, such as, for example, S, N or O.

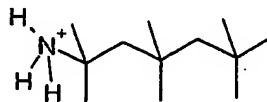
Examples of especially preferred ammonium cations are:

- unsubstituted ammonium,
- mono-, di-, tri- or tetra- $C_{1-4}$ alkylammonium, such as methylammonium, ethylammonium, 3-propylammonium, isopropylammonium, butylammonium, sec-butylammonium, isobutylammonium, 1,2-dimethylpropylammonium or 2-ethylhexylammonium, dimethylammonium, diethylammonium, dipropylammonium, diisopropylammonium, dibutylam-



monium, diisobutylammonium, di-sec-butylammonium, di-2-ethylhexyl-ammonium, N-methyl-n-butylammonium or N-ethyl-n-butylammonium, trimethyl- or triethyl-ammonium, tripropylammonium, tributylammonium, N,N-dimethylethyl-ammonium, N,N-dimethylisopropylammonium, N,N-dimethylbenzylammonium or

5  $(\text{CH}_3)_2((\text{CH}_3\text{O})_2\text{CHCH}_2)\text{NH}^+$ ,



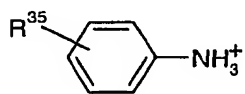
- mono-, di-, tri- or tetra- $\text{C}_{8-16}$ alkylammonium, such as (idealised representation of the ammonium cation of Primene 81R®),

-  $\text{C}_{1-4}$ alkoxy- $\text{C}_{1-4}$ alkylammonium, such as 2-methoxyethylammonium, bis(2-methoxyethyl)ammonium, 3-methoxypropylammonium or ethoxypropylammonium,

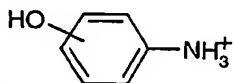
10 - mono-, di- or tri-(hydroxy- $\text{C}_{1-4}$ alkyl)ammonium, such as mono-, di- or tri-ethanolammonium, mono-, di- or tri-isopropanolammonium, N-methyl- or N,N-dimethyl-ethanolammonium, -propanolammonium or -isopropanolammonium, N-methyl-diethanolammonium, -dipropanolammonium or -diisopropylammonium, N-ethyl-diethanolammonium, -dipropanolammonium or -diisopropylammonium, N-propyl-

15 diethanolammonium, -dipropanolammonium or -diisopropylammonium, - N-(2-hydroxyethyl)pyrrolidinium, N-(2- or 3-hydroxypropyl)pyrrolidinium, N-(2-hydroxyethyl)piperidinium, N-(2- or 3-hydroxypropyl)piperidinium, N-(2-hydroxyethyl)morpholinium, N-(2- or 3-hydroxypropyl)morpholinium or N-(2-hydroxyethyl)-piperazinium,

20 and



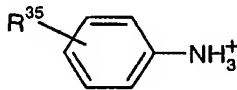
, especially



, such as 2-, 3- or 4-hydroxy-

phenylammonium, wherein  $\text{R}^{35}$  is a hydroxy group, a  $\text{C}_{1-8}$ alkoxy group, a carboxylic acid group or  $\text{COOR}^{36}$ , wherein  $\text{R}^{36}$  is a  $\text{C}_{1-8}$ alkyl group, a  $\text{C}_{6-10}$ aryl group or a  $\text{C}_{7-11}$ aralkyl group. Tetramethylammonium and tetraethylammonium salts are especially suitable for

25 inkjet printing. Ammonium cations of formula



can contribute to an increase in fastness to light.

Also suitable are polyammonium salts, especially diammonium compounds. Preferred diammonium compounds are derived from the following amines: 1,2-diaminoethane, 1,2-diamino-1-methylethane, 1,2-diamino-1,2-dimethylethane, 1,2-diamino-1,1-dimethyl-

30 ethane, 1,2-diaminopropane, 1,3-diaminopropane, 1,3-diamino-2-hydroxypropane, N-

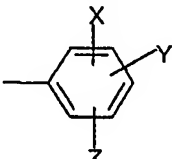
methyl-1,2-diaminoethane, 1,4-diazacyclohexane, 1,2-diamino-1,1-dimethylethane, 2,3-diaminobutane, 1,4-diaminobutane, N-hydroxyethyl-1,2-diaminoethane, 1-ethyl-1,3-diaminopropane, 2,2-dimethyl-1,3-diaminopropane, 1,5-diaminopentane, 2-methyl-1,5-diaminopentane, 2,3-diamino-2,3-dimethylbutane, N-2-aminoethylmorpholine, 1,6-  
 5 diaminohexane, 1,6-diamino-2,2,4-trimethylhexane, N,N-dihydroxyethyl-1,2-diaminoethane, N,N-dimethyl-1,2-diaminoethane, 4,9-dioxo-1,12-diaminododecane, 1,2-diaminocyclohexane, 1,3-diamino-4-methylcyclohexane, 1,2-diaminocyclohexane, 1-amino-2-aminomethyl-2-methyl-4,4-dimethylcyclohexane, 1,3-diaminomethylcyclohexane, N-2-aminoethylpiperazine, 1,1-di(4-aminocyclohexyl)methane, 1,1-di(4-amino-  
 10 phenyl)methane, N,N'-diisopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methyl-heptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-di(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-  
 15 dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine and N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine.

In the groups  $-OR^1$ ,  $-SR^2$ ,  $-C(O)OR^3$  and  $-C(O)R^4$ ,  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  can have, *inter alia*, the following meanings:

20  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  as  $C_{1-4}$ alkyl are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl, preferably methyl or ethyl, and as  $C_{6-12}$ aryl are phenyl, biphenyl or naphthyl, preferably phenyl.

In the group  $-NR^5R^6$ ,  $R^5$  and  $R^6$  are, in addition to a hydrogen atom, a  $C_{1-4}$ alkyl radical, e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl, preferably  
 25 methyl or ethyl, or a radical  $-(CH_2)_oOH$ , wherein o is an integer from 1 to 6, especially 2 or 3, and the nitrogen atom is preferably symmetrically substituted.

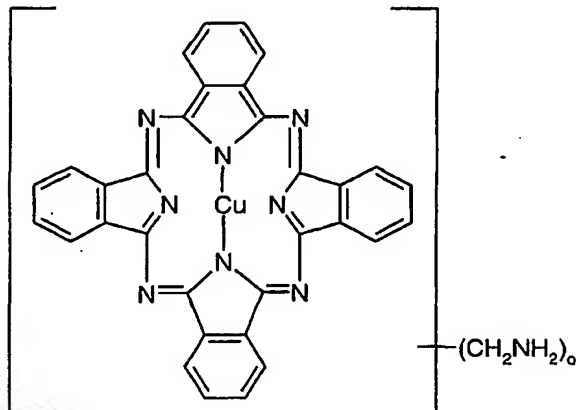
B and B' are especially preferably selected from the following groups:

a hydrogen atom,  $-(CH_2)_e-E$  and , wherein e is an integer from 1 to 6,

30 especially 2 or 3, E is a hydrogen atom, a group  $-OH$ ,  $-OCat$ ,  $-SH$ ,  $-SCat$ ,  $-OR^1$ ,  $-SR^2$ ,  $-NR^5R^6$  or  $-C(O)OR^3$ , and X, Y and Z are each independently of the others selected from a hydrogen atom and a group  $-OH$ ,  $-OCat$ ,  $-SH$ ,  $-SCat$ ,  $-OR^1$ ,  $-SR^2$ ,  $-NR^5R^6$  and  $-C(O)OR^3$ , wherein  $R^1$ ,  $R^2$  and  $R^3$  are each independently of the others a  $C_{1-4}$ alkyl radi-

cal, especially methyl or ethyl, and  $R^5$  and  $R^6$  denote a radical  $-(CH_2)_oOH$ , wherein  $o$  is an integer from 2 to 6, and Cat is a sodium or potassium cation, unsubstituted ammonium or an ammonium cation described hereinbefore as preferred.

$A'$  is the radical of a chromophore that already contains one or more primary amino groups, such as 1-aminoanthraquinone, or is one of the chromophore radicals listed under A substituted by from 1 to 8, preferably by from 1 to 4, amino groups, such as, for example,



, wherein  $o$  denotes a value from 1 to 8,

preferably from 1 to 4 (see EP-A-311 562).

- 10 A is the radical of a known chromophore having the basic structure  $A(H)_{m+n}$ . Examples of such chromophores are described, for example, in W. Herbst, K. Hunger, Industrielle Organische Pigmente, 2nd completely revised edition, VCH 1995. In principle, all chromophores whose basic structure can be modified with one or more sulfonamide groups are suitable. The chromophore is usually selected from the series 1-amino-
- 15 anthraquinone, anthraquinone, anthrapyrimidine, azo, azomethine, benzodifuranone, quinacridone, quinacridonequinone, quinophthalone, diketopyrrolopyrrole, dioxazine, flavanthrone, indanthrone, indigo, isoindoline, isoindolinone, isoviolanthrone, perinone, perylene, phthalocyanine, pyranthrone or thioindigo.

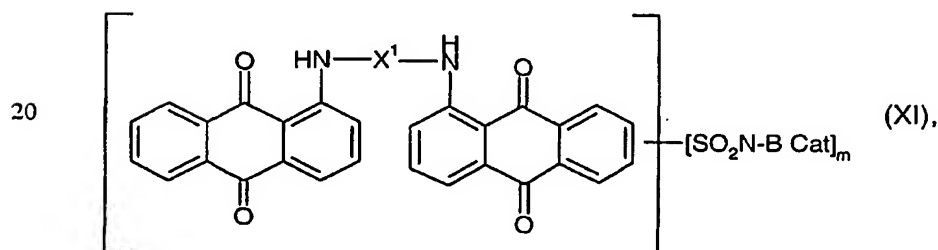
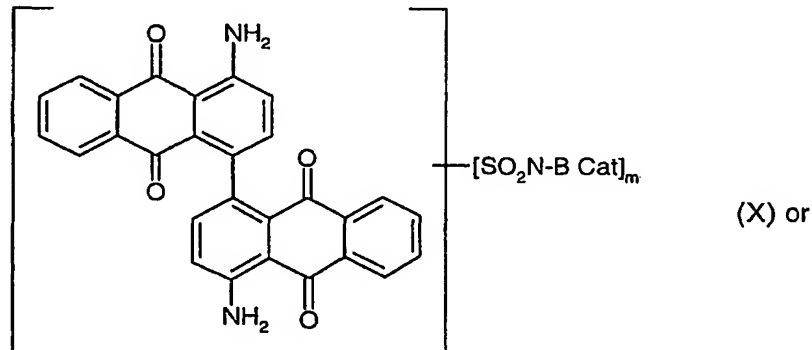
- Examples of pigments (and substituted derivatives thereof) that can be used as starting
- 20 compound for the sulfonamide salts according to the invention and that come under the classes of pigments mentioned above are described in W. Herbst, K. Hunger, Industrielle Organische Pigmente, 2nd completely revised edition, VCH 1995: 1-amino-anthraquinone pigments: p. 503-511; anthraquinone pigments: p. 504-506, 513-521 and 521-530; anthrapyrimidine: p. 513-415; azo pigments: p. 219-324 and 380-398; azomethine pigments: p. 402 - 411; quinacridone pigments: p. 462-481; quinacridonequinone
- 25 pigments: p. 467-468; quinophthalone pigments: p. 567-570; diketopyrrolopyrrole pig-


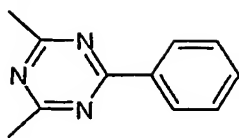
ments: p. 570-574; dioxazine pigments: p. 531-538; flavanthrone pigments: p. 517-519, 521; indanthrone pigments: p. 515-517; isoindoline pigments: p. 413-429; isoindolinone pigments: p. 413-429; isoviolanthrone pigments: p. 528-530; perinone pigments: p. 482-492; perylene pigments: p. 482-496; phthalocyanine pigments: p. 431-460; pyranthrone pigments: p. 522-526; thioindigo pigments (indigo pigments): p. 497-500, it also being possible to use mixtures of such pigments, including solid solutions.

Depending on the intended use, generally only some of the sulfonamide groups may be converted to the salt form. In the pigmenting of wood, it is preferred according to the invention to convert practically all of the sulfonamide groups present in the molecule into the salt form, that is to say in formulae I and II  $n$  and  $n'$  are 0, whereas in the pigmenting of anodised aluminium it may be advantageous, for the purpose of obtaining a suitable pH value, to convert only some of the sulfonamide groups into the salt form, that is to say in formulae I and II  $n$  and  $n'$  are  $\geq 1$ .

Colorants of formula I are preferred to those of formula II.

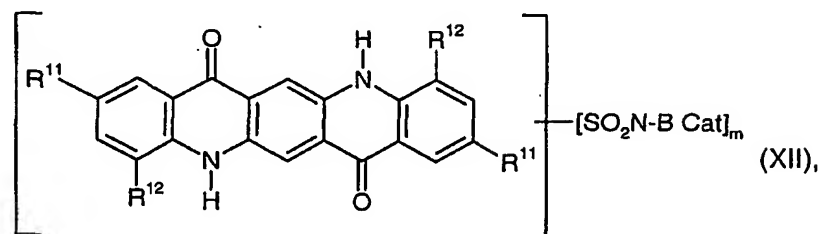
- 15 Of the colorants of formula I, preference is given to the following, wherein B is as defined above and Cat is an alkali metal cation, especially a sodium or potassium cation, unsubstituted ammonium or an ammonium cation described hereinbefore as preferred:
- salts of 1-aminoanthraquinone and anthraquinone pigments of formula



wherein  $X^1$  is a group  or  and m denotes a value

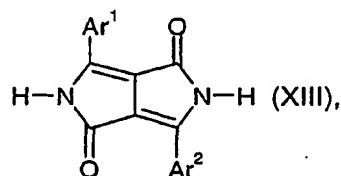
from 1 to 4, especially from 2 to 3;

- salts of quinacridone pigments of formula

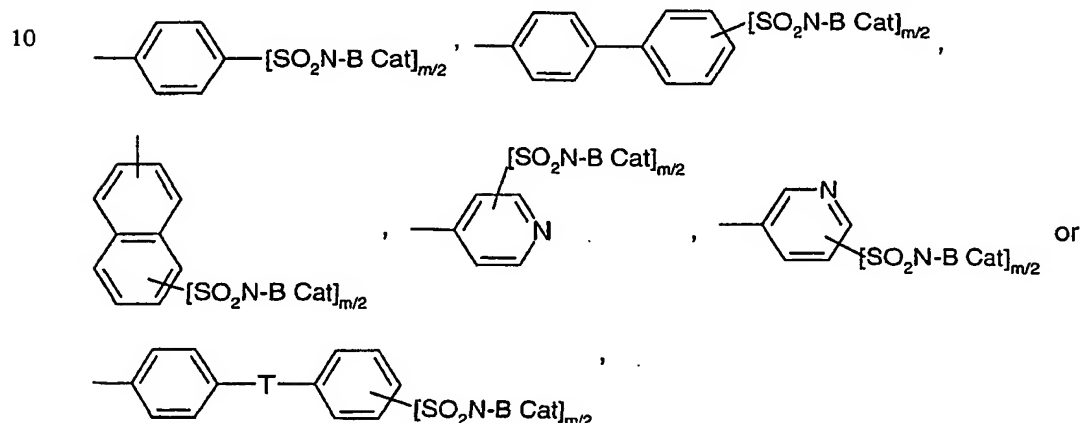


- 5 wherein  $R^{11}$  and  $R^{12}$  are each independently of the other hydrogen, halogen,  $C_1$ - $C_{24}$ alkyl,  $C_1$ - $C_6$ alkoxy or phenyl and m denotes a value from 1 to 4, especially from 2 to 3;

- salts of pyrrolo[3,4-c]pyrroles of formula



wherein  $Ar^1$  and  $Ar^2$  are each independently of the other a group of formula

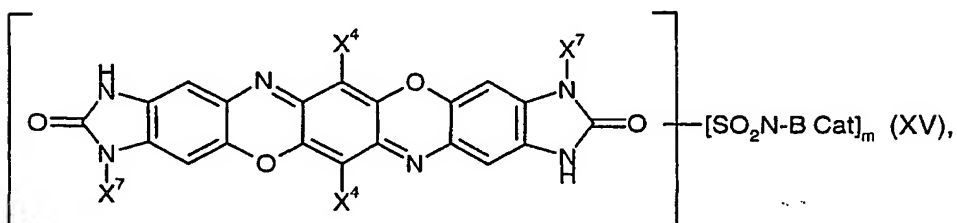
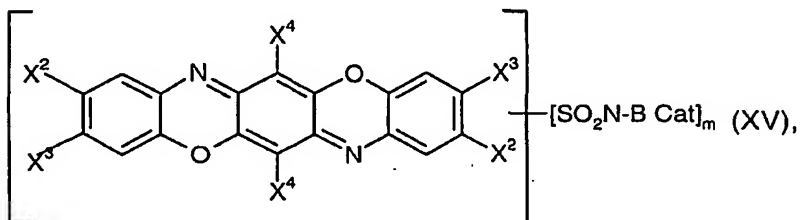
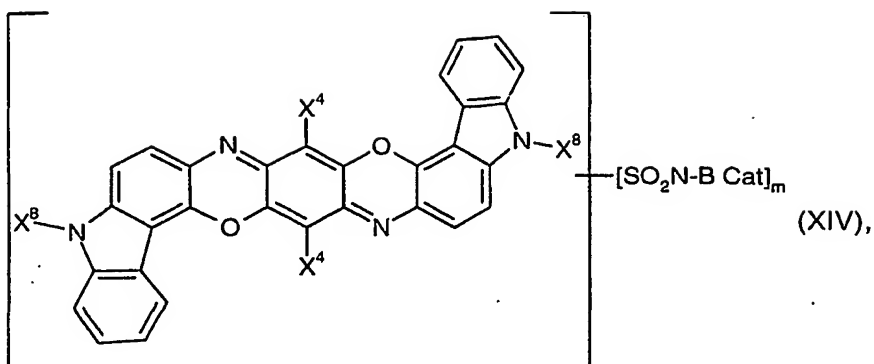


wherein T is  $-CH_2-$ ,  $-CH(CH_3)-$ ,  $-C(CH_3)_2-$ ,  $-CH=N-$ ,  $-N=N-$ ,  $-O-$ ,  $-S-$ ,  $-SO-$ ,  $-SO_2-$  or  $-NR^{13}$ , wherein  $R^{13}$  is hydrogen or  $C_1$ - $C_6$ alkyl, especially methyl or ethyl, and m denotes a

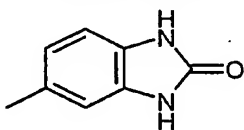
- 15 value from 1 to 4, especially from 2 to 3;

- salts of dioxazines of formula

13

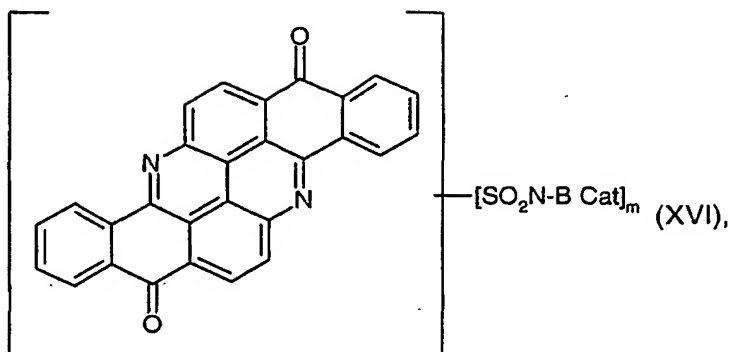


- wherein  $X^2$  is a  $C_{1-4}$ alkoxy radical, especially ethoxy,  $X^3$  is a  $C_{1-4}$ acylamino group, especially an acetylamino group, or a benzoylamino group and  $X^4$  is a chlorine atom or a radical  $NHC(O)CH_3$ ,  $X^7$  is a hydrogen atom, a  $C_{1-8}$ alkyl radical, a substituted or unsubstituted phenyl, benzyl, benzanilide or naphthyl group, a  $C_{5-7}$ cycloalkyl radical or a radical



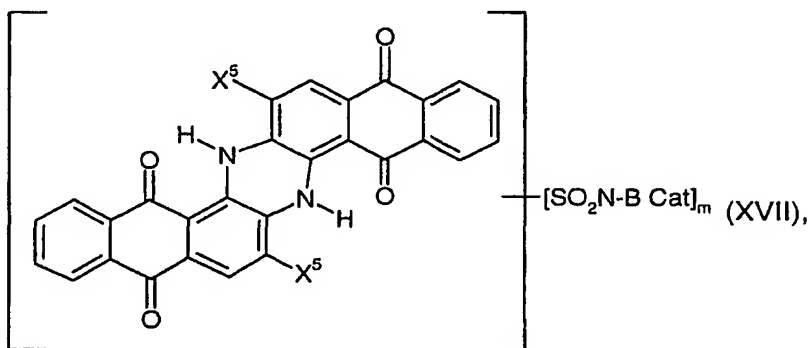
of formula ,  $X^8$  is a hydrogen atom or a  $C_{1-4}$ alkyl radical and m denotes a value from 1 to 4;

- 10 - salts of flavanthrones of formula



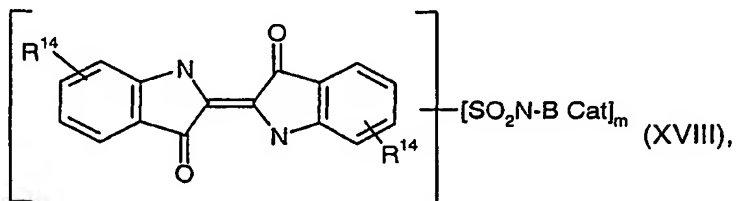
wherein m denotes a value from 1 to 4, especially from 2 to 3;

- salts of indanthrones of formula



5 wherein X<sup>5</sup> is a hydrogen or chlorine atom and m denotes a value from 1 to 4, preferably from 2 to 3;

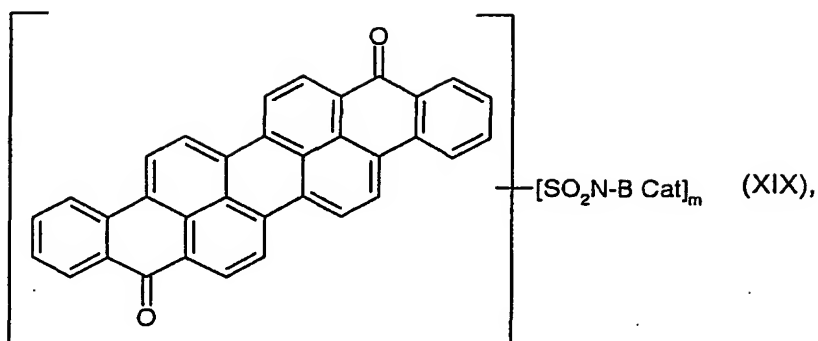
- salts of indigo derivatives of formula



10 wherein R<sup>14</sup> is hydrogen, CN, C<sub>1-6</sub>alkyl, C<sub>1-6</sub>alkoxy or halogen and m denotes a value from 1 to 3;

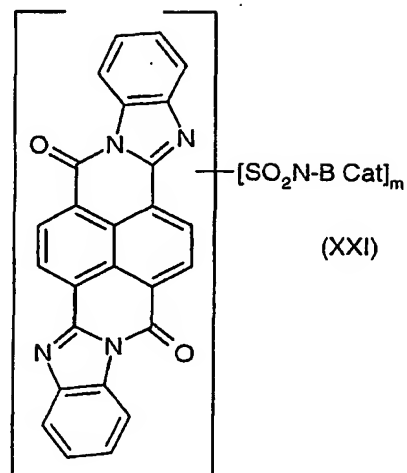
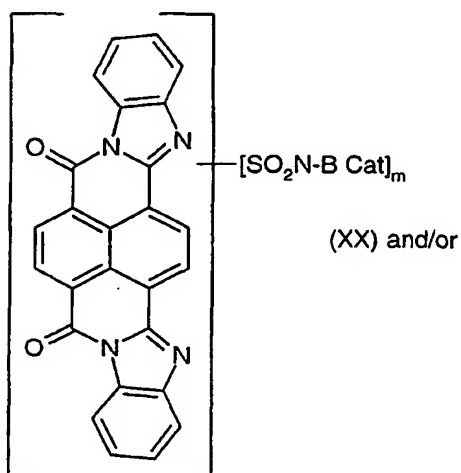
- salts of isoviolanthrone:

15



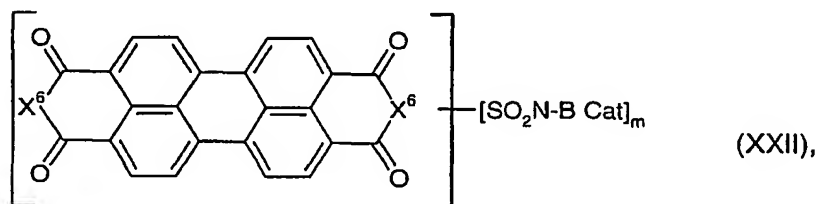
wherein m denotes a value from 1 to 4;

- salts of perinone pigments of formula



5 wherein m denotes a value from 1 to 4;

- salts of perylene pigments of formula



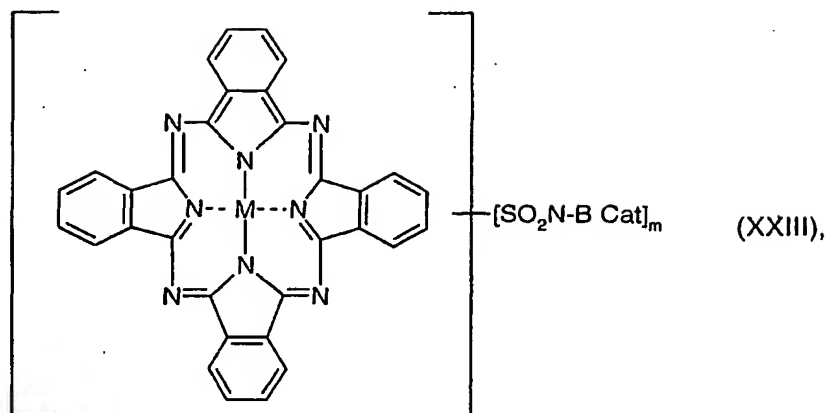
in which  $X^6$  is O or  $NR^{15}$ ,  $R^{15}$  being H,  $CH_3$  or unsubstituted or substituted phenyl or

10  $C_{7-11}$ alkyl, such as benzyl or 2-phenylethyl, and m denotes a value from 1 to 4, especially from 2 to 3, it being possible for the phenyl ring to be substituted by methyl, methoxy, ethoxy or by  $-N=N-Ph$ ;

- salts of phthalocyanines of formula



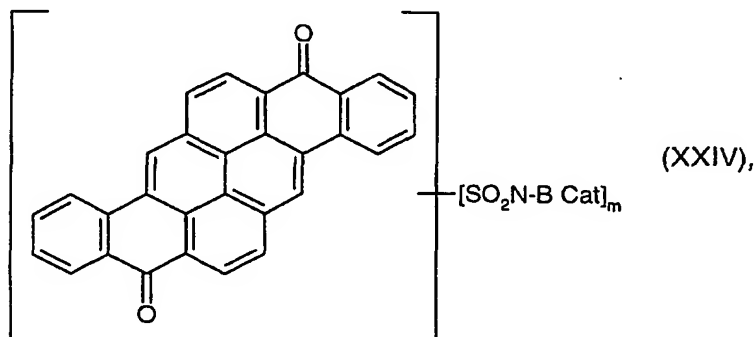
16



wherein M is H<sub>2</sub>, a bivalent metal selected from the group Cu(II), Zn(II), Fe(II), Ni(II), Ru(II), Rh(II), Pd(II), Pt(II), Mn(II), Mg(II), Be(II), Ca(II), Ba(II), Cd(II), Hg(II), Sn(II), Co(II) and Pb(II), or a bivalent oxo metal selected from the group V(O), Mn(O) and TiO, and m

5 denotes a value from 2 to 6, especially from 3 to 5;

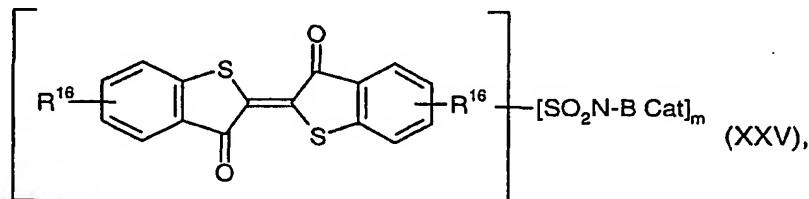
- salts of pyranthrone pigments of formula



and bromo-, chloro- or bromo- and chloro-halogenated derivatives of the basic structure, for example the 2,10-dichloro, 4,6- and 6,14-dibromo derivatives, wherein m denotes a

10 value from 2 to 4,

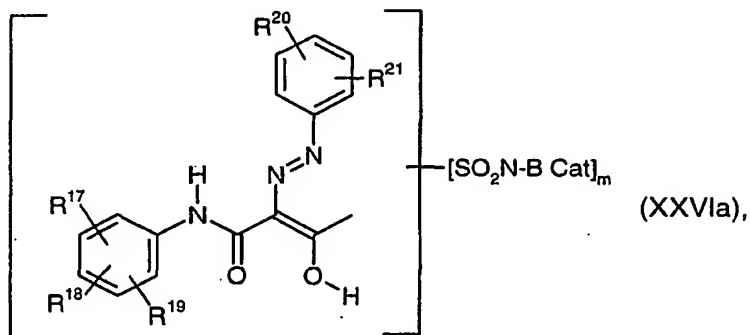
- salts of thioindigo derivatives of formula



wherein R<sup>16</sup> is hydrogen, CN, C<sub>1-6</sub>alkyl, especially methyl, C<sub>1-6</sub>alkoxy, especially methoxy, or halogen, especially chlorine, and m denotes a value from 1 to 3,

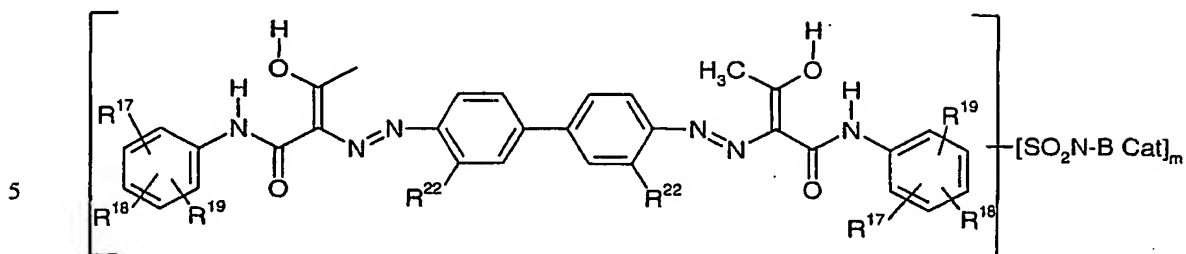
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- salts of monoazo yellow and orange pigments of formula

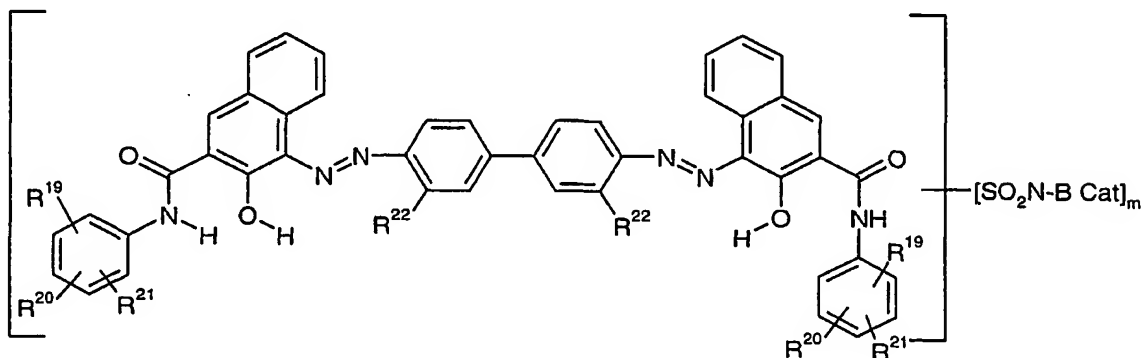


wherein m denotes a value from 1 to 4,

- salts of diaryl yellow pigments of formula



- salts of naphthol AS pigments of formula



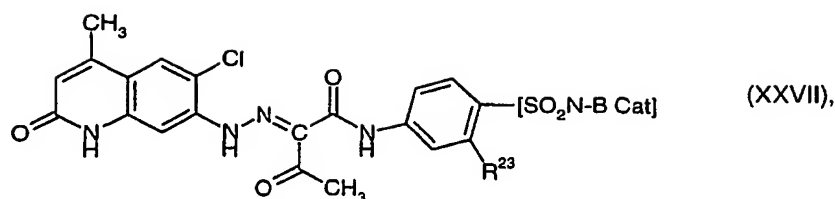
R<sup>17</sup> to R<sup>21</sup> are each independently of the others a hydrogen atom, a halogen atom,

C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>alkoxy, a nitro group or an acetyl group,

R<sup>22</sup> is a hydrogen atom, a halogen atom, C<sub>1-6</sub>alkyl or C<sub>1-6</sub>alkoxy,

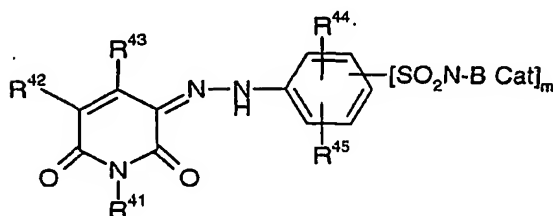
- salts of monoazoquinolone pigments of formula

18



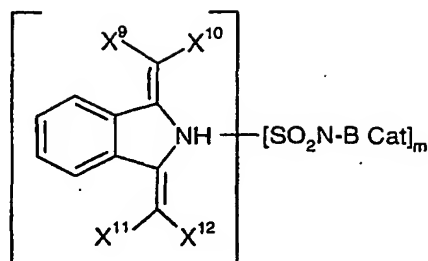
wherein  $R^{23}$  is hydrogen, halogen,  $C_{1-4}$ alkyl,  $C_{1-4}$ alkoxycarbonyl,  $C_{1-4}$ alkylcarbonyl,  $C_{1-4}$ alkanoylamino (the preparation of monoazoquinolone pigments is described in EP01/12178), and

- 5 - salts of azo pigments of formula



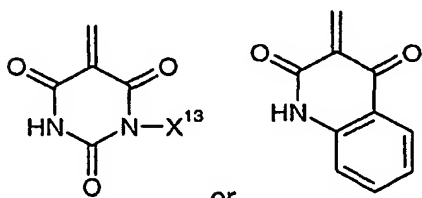
(XXVIII), wherein

- $R^{41}$  is a hydrogen atom, a  $C_{1-4}$ alkyl radical, such as methyl or ethyl, or a perfluoro- $C_{1-4}$ alkyl radical, such as trifluoromethyl, a hydroxy- $C_{1-4}$ alkyl radical or a  $C_{1-8}$ alkyl radical interrupted one or more times by -O-, such as  $CH_2CH_2CH_2-O-CH(CH_3)_2$ , a  $C_{6-10}$ aryl radical, such as phenyl, or a  $C_{7-12}$ aralkyl radical, such as benzyl,
- $R^{42}$  is a hydrogen atom, or a cyano or carbonamide group,
- $R^{43}$  is a hydrogen atom, a carboxylic acid group or a salt thereof or a  $C_{1-4}$ alkyl radical,
- $R^{44}$  and  $R^{45}$  denote a  $C_{1-4}$ alkyl radical, such as methyl or ethyl, a perfluoro- $C_{1-4}$ alkyl radical, such as trifluoromethyl, a  $C_{1-4}$ alkoxy radical, such as methoxy or ethoxy, a nitro group, a halogen atom, such as chlorine,  $COOR^{46}$ , wherein  $R^{46}$  is a  $C_{1-4}$ alkyl radical, a  $C_{6-10}$ aryl radical that is unsubstituted or substituted, for example by one or two chlorine atoms, such as phenyl or 1,4-dichlorophenyl, or a  $C_{7-12}$ aralkyl radical, such as benzyl,  $CONHR^{47}$ , wherein  $R^{47}$  is a  $C_{1-4}$ alkyl radical, a  $C_{6-10}$ aryl radical, such as phenyl, or a  $C_{7-12}$ aralkyl radical, such as benzyl, and  $m$  denotes a value from 1 to 2,
- 20 - salts of isoindoline pigments of formula



(XXIX), wherein

$X^9$ ,  $X^{10}$ ,  $X^{11}$  and  $X^{12}$  are CN, CONH- $C_{1-8}$ alkyl or CONH- $C_{6-10}$ aryl or  $X^9$  and  $X^{10}$  and/or  $X^{11}$  and  $X^{12}$  are each members of a heterocyclic ring, such as

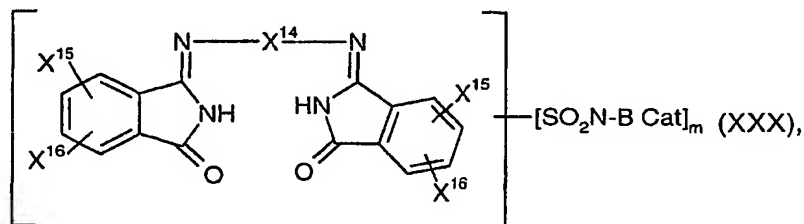


or

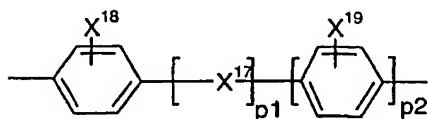
, wherein  $X^{13}$  is a hydrogen atom or a  $C_{6-10}$ aryl radical,

5 and m denotes a value from 1 to 4,

- salts of isoindoline pigments of formula



wherein  $X^{14}$  is the radical of an aromatic or heteroaromatic diamine, such as

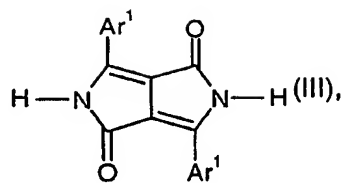


, wherein p1 and p2 are 0 or 1,  $X^{18}$  and  $X^{19}$  are a

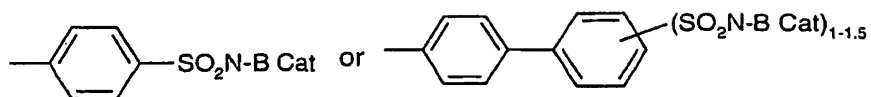
10 hydrogen atom, a  $C_{1-4}$ alkyl radical, a  $C_{1-4}$ alkoxy radical or a chlorine atom,  $X^{17}$  is a group -CH<sub>2</sub>-, -CH=CH- or -N=N-,  $X^{15}$  and  $X^{16}$  are a hydrogen atom, a  $C_{1-4}$ alkyl radical, a  $C_{1-4}$ alkoxy radical, a nitro group or a chlorine atom and m denotes a value from 1 to 3, and B and Cat are as defined above.

Preferred colorants are:

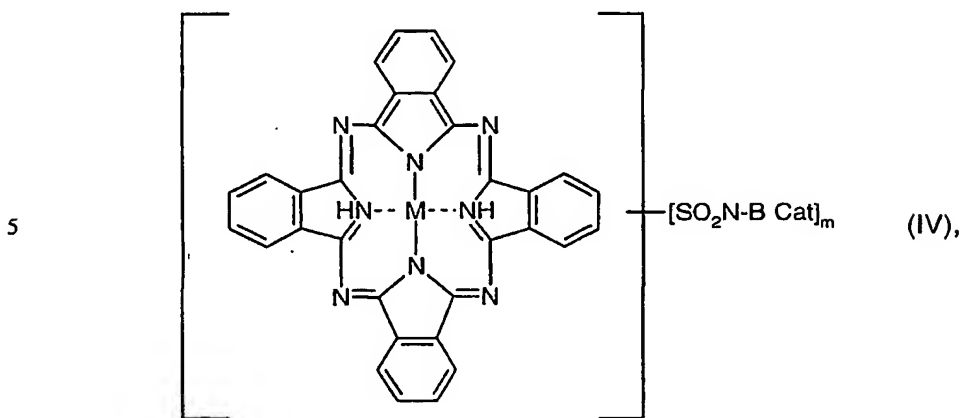
15 - pyrrolo[3,4-c]pyrrole derivatives of formula



wherein Ar<sup>1</sup> is a group of formula

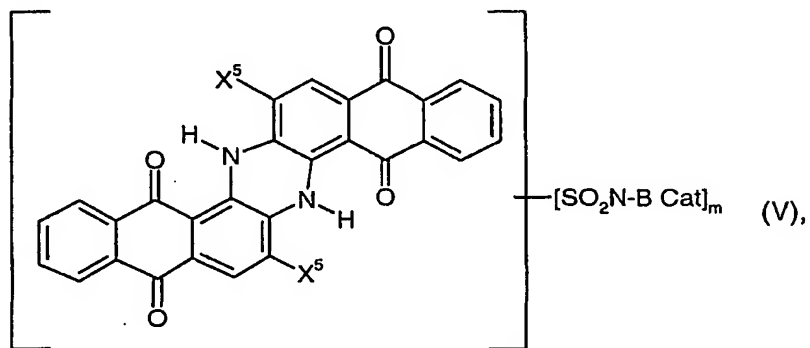


- phthalocyanine derivatives of formula



wherein M is Cu(II) or Zn(II), and m denotes a value from 3 to 5,

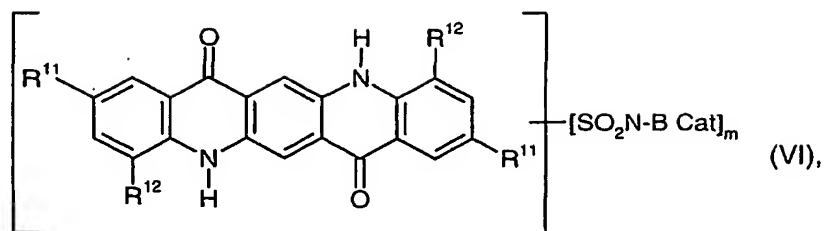
- indanthrone derivatives of formula



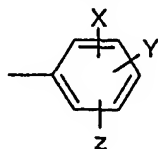
wherein X<sup>5</sup> is a hydrogen or chlorine atom and m denotes a value from 2 to 4, and

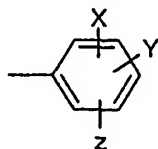
10 - quinacridone derivatives of formula

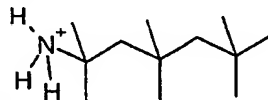
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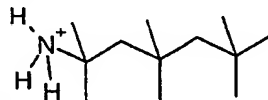


wherein  $R^{11}$  and  $R^{12}$  are each independently of the other hydrogen, a chlorine atom or a methyl group,  $m$  denotes a value from 1 to 4 and



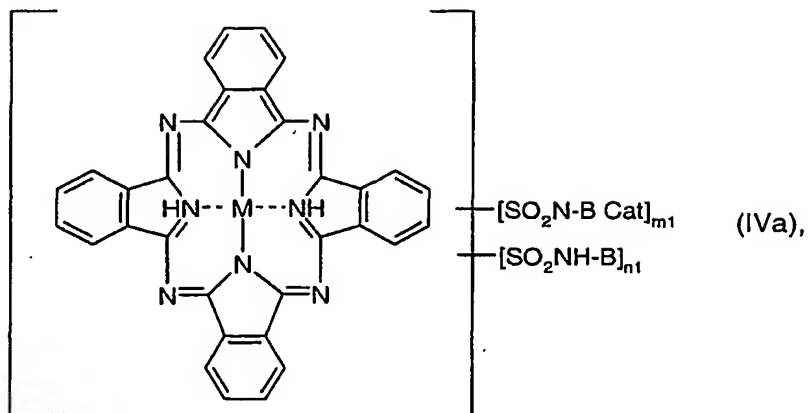
- B is a group  $-(CH_2)_e-E$  or , wherein  $e$  is an integer from 1 to 6, especially 2 or 3,  $E$  is a hydrogen atom or a group  $-OH$ ,  $-OCat$ ,  $-SH$ ,  $-SCat$ ,  $-OR^1$ ,  $-SR^2$ ,  $-NR^5R^6$  or  $-C(O)OR^3$ , and  $X$ ,  $Y$  and  $Z$  are each independently of the others selected from a hydrogen atom and a group  $-OH$ ,  $-OCat$ ,  $-SH$ ,  $-SCat$ ,  $-OR^1$ ,  $-SR^2$ ,  $-NR^5R^6$  and  $-C(O)OR^3$ , wherein  $R^1$ ,  $R^2$  and  $R^3$  are each independently of the others a  $C_{1-4}$ alkyl radical, especially methyl or ethyl, and  $R^5$  and  $R^6$  denote a radical  $-(CH_2)_oOH$ , wherein  $o$  is an integer from 2 to 6, especially 2 or 3, and  $Cat$  is a sodium or potassium cation or unsubstituted ammonium or an ammonium cation described hereinbefore as preferred, especially tetra-



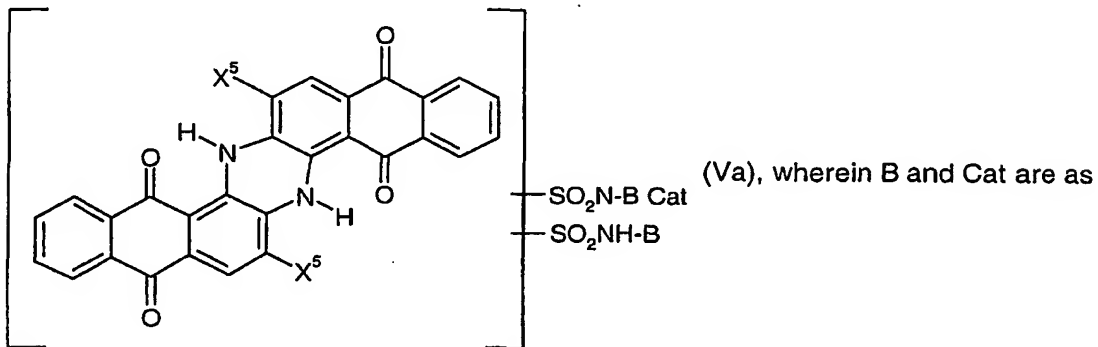
methylammonium; tetraethylammonium or , mono-, di- or tri-ethanolammonium or mono-, di- or tri-isopropanolammonium, N-methyl-N-ethanolammonium or 2-, 3- or 4-hydroxyphenylammonium.

- In the above formulae III to VI and X to XXX one to three groups  $-SO_2NBCat$  can be replaced by groups  $-SO_2NHB$  with the proviso that at least one group  $-SO_2NBCat$  is present. Examples of compounds modified in such a way are sulfonamide salts of the following formulae (IVa), (Va) and (Xa) and of formula (IVb) below:

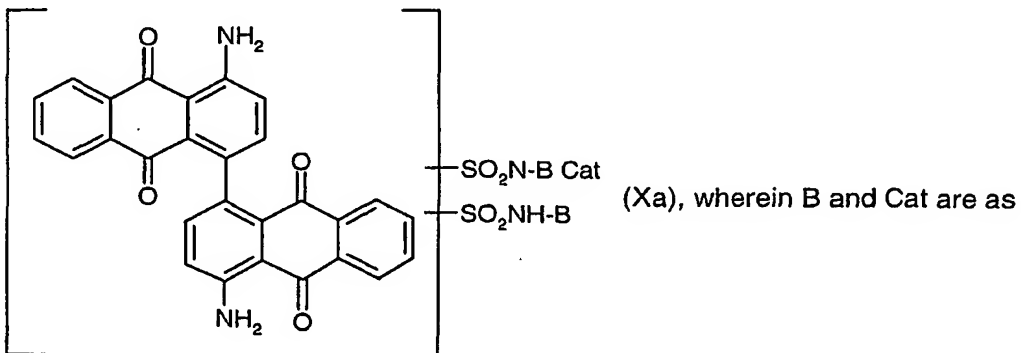
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wherein M, Cat and B are as defined in formula IV,  $m_1$  and  $n_1$  denote a value from 1 to 4, especially 1 to 3, wherein the sum of  $m_1$  and  $n_1$  being 3 to 5, especially 4,



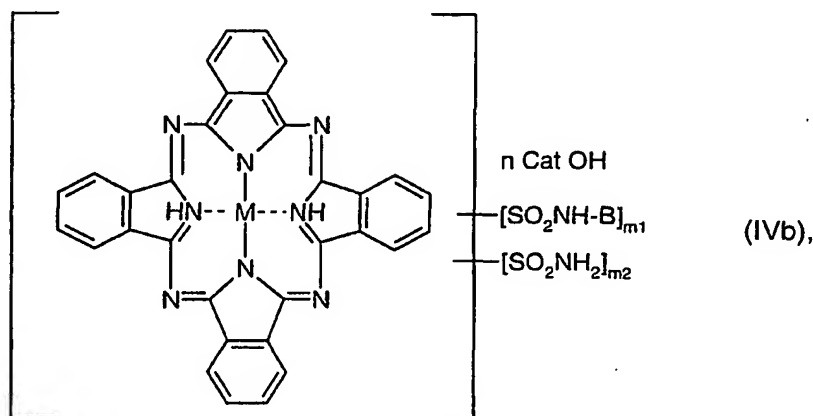
5 defined in formula V, and



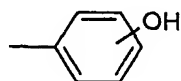
defined in formula X.

Sulfonamide derivatives in which  $-\text{SO}_2\text{NHB}/-\text{SO}_2\text{NB}$  is either  $-\text{SO}_2\text{NH}_2/-\text{SO}_2\text{NH}$  or a mixture of  $-\text{SO}_2\text{NH}_2/-\text{SO}_2\text{NH}$  and  $-\text{SO}_2\text{NHB}/-\text{SO}_2\text{NB}$  are especially suitable for the pig-

menting of aluminium. Examples of such derivatives are phthalocyanine derivatives of formula



wherein M is Cu(II) or Zn(II), m1 denotes a value from 0 to 3, m2 denotes a value from 1 to 4, the sum of m1 and m2 being 3 to 5, especially 4, n denotes a value from 1 to 8, B



is a group  $-(CH_2)_e-E$  or  $-\text{C}_6\text{H}_4-\text{OH}$ , wherein e is an integer 2 or 3, E is a hydrogen atom, a group  $-OH$ ,  $-SH$ ,  $-OR^1$ ,  $-SR^2$ ,  $-NR^5R^6$  or  $-C(O)OR^3$ , and Cat is a sodium or potassium cation or unsubstituted ammonium or an ammonium cation described hereinbefore as preferred.

The colorants are derived especially from C. I. Pigment Yellow 138, 139, 185, C.I. Pigment Brown 38, C.I. Pigment Orange 66, 69, C.I. Pigment Red 260; C. I. Pigment Red 123, 149, 178, 179, 190, 224, C.I. Pigment Violet 29, C.I. Pigment Black 31, 32; C.I. Pigment Blue 15:6; C.I. Pigment Violet 19, C.I. Pigment Red 122, 192, 202, 207 and 209; C.I. Pigment Red 254, C.I. Pigment Red 255, C.I. Pigment Red 264, C.I. Pigment Red 272, C.I. Pigment Orange 71, C.I. Pigment Orange 73; C.I. Pigment Blue 60 and 64; C.I. Pigment Violet 29, C.I. Pigment Red 123, 179, 190 or C.I. Pigment Violet 23 or 37.

Especially preferred as colorants of formula I are the compounds A1, A2, B1 to B5, C1 to C8, D1 to D55, E1 to E8, F1 and G1 to G3 listed in the Examples, compounds D4, D39, D53 and E1 to E8 being especially suitable for the pigmentation of wood, whilst compounds D54 and D55 yield very good results in the coloration of aluminium. For shade matching or to produce intermediate colours, it is also possible to use mixtures of colorants of formula I and/or II for the coloration. To produce colour effects, it is possible for a plurality of colorants of formula I or II to be deposited in succession into the pores of the porous materials.



Preferably, the colorants according to the invention do not contain deprotonatable carboxylic acid groups or sulfonic acid groups or benzimidazole radicals.

5 The colorants of formulae I and II according to the invention can be obtained from the corresponding sulfonamides by reaction with alkali metal hydroxides or ammonium hydroxides or amines. The sulfonamides that are used as starting materials are either known (see e.g. GB-A-1 198 501, US-A-4 234 486, US-A-6 066 203 etc.) or can be prepared according to known processes (see e.g. US-A-6 066 203, 3rd column, lines 36 to 50). In the case of the colorants of formula I, the pigment is advantageously reacted  
10 with chlorosulfonic acid/thionyl chloride to form the pigment sulfonyl chloride, which is then reacted with the corresponding amine to form the sulfonamide.

The colorants of formula II can be obtained, for example, by nitrating a starting pigment, reducing the resulting nitro groups and reacting the resulting amino groups with the corresponding sulfonic acid chloride, or by using processes known *per se* to introduce  
15 aminomethyl groups into the starting pigments (see EP-A- 311 562) and to react the amino groups with the corresponding sulfonic acid chloride.

The present invention relates also to the use of the colorants of the general formulae I and II for the pigmenting of porous materials, especially for the pigmenting of wood and anodised aluminium in the pores, and in inkjet printing.

20 The colorants according to the invention can be used individually or in mixtures with other colorants or, for example, dyes customary for the application in question.

The colorants of the invention are generally used in an amount effective for pigmenting, that is to say in an amount that is sufficient to bring about a colour difference  $\Delta E^*$

( $CIE-L^*a^*b^*$ )  $\geq 2$  when the pigmented material is compared with the unpigmented material using standard light type  $D_{65}$  at an observation angle of  $10^\circ$ . The amount is preferably from 0.01 to 30 % by weight, especially from 0.1 to 15 % by weight, based on the  
25 weight of the pigmented material.

The porous materials may be of natural or synthetic origin, and may be mineral or organic. Examples of porous materials are porous metal oxides, such as the oxides of  
30 elements of groups 2, 3, 4, 12, 13 and 14 of the Periodic Table, for example oxides of aluminium, silicon, magnesium and mixtures thereof, especially anodised light metals, especially aluminium, or alloys thereof, and porous synthetic materials, for example porous polyamide fillers, especially polyamide-12, polyamide-6 or co-polyamide-6/12 fillers, the manufacture of which is described in US-A-4 831 061, FR-A-2 619 385 and  
35 EP-A-303 530 and which are sold by Atofina under the trade name Orgasol®. Further

examples of porous materials are chalk, pumice, calcined clay, unglazed ceramics, gypsum, concrete, kieselguhr, silica gel, zeolites, wood, paper, leather, imitation leather and hair. The colorants according to the invention are suitable especially for pigmenting wood and anodised aluminium.

5 The principle according to the invention will now be described taking the example of wood and aluminium. It is clear, however, that with slight modifications the principle can be transferred to any other desired porous materials.

Wood is especially any kind of hard or soft wood, for example obeche, ash, birch, poplar, pine, spruce, fir, tulip tree, maple, bird's eye maple, sycamore, oak, beech, mahogany, myrtle, anigre, tay (koto), mappa burl, elm, zebrano, carbalho, vavona or daniela. The methods and conditions for treating wood and wood products are known from the specialist literature, to which reference is expressly made herein. For example, the methods and conditions for treatment with solutions are described in detail in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A28, 305-393 (5th edition 1996) and in Kirk-  
10 Othmer Encyclopedia of Chemical Technology, Vol. 24, 579-611 (3rd edition 1978). The application temperature can be elevated but it is advantageous to keep it sufficiently low that decomposition of the colorant does not occur, or occurs only negligibly, during the minimum time required for application. Where appropriate, it is also possible to add to the colorant solution further substances known for the treatment of the material, for  
15 example fungicides, antibiotics, flame retardants or moisture repellants.

If, when pigmenting wood, the colorants are used in admixture, then the components of the mixture are preferably components, the colour of which in the pigmentary form is red, yellow, blue, green, brown or black. Brown shades of an especially natural appearance can be produced therefrom. Any colorants added thereto are also preferably red,  
20 yellow, blue, green, brown or black.

According to the invention water is used as solvent. Where appropriate, co-solvents may be used, such as alcohol, for example ethanol or propanol, ethers, for example diethyl ether or methoxypropanol, or ketones, for example acetone or methyl ethyl ketone, the amount thereof generally not exceeding 15 % by weight, preferably not exceeding 10 %  
30 by weight. It is especially preferred to use water alone as solvent.

The concentration of the colorant in water is customarily from 0.01 % by weight to about 99 % of the saturation concentration, although in some cases it is possible to use supersaturated solutions without premature precipitation of the salt. For many colorants, the optimum concentration is about from 0.05 to 10 % by weight, often about from 0.1 to 5  
35 % by weight, colorant, based on water. The solution of the compounds of formula (I) generally has a pH of from 6 to 11. The pH will depend, *inter alia*, upon the material to

be coloured; for example, for wood it is preferably from 8 to 10, and for aluminium preferably from 6 to 8.

The pH of the aqueous solutions of the sulfonamide salts can be adjusted by specific selection of the following parameters:

- 5 - nature of groups B and B',
- number of groups [SO<sub>2</sub>-N-B] and/or [N-SO<sub>2</sub>-B] and
- nature of cations Cat.

For example, compounds D17, D46, D54 and D55 have a pH of 6 to 7 and are accordingly especially suitable for pigmenting aluminium.

- 10 In order to obtain a desired pH within the range from 6 to 11, there may also be used, for example, buffer solutions based on borax, Tris buffer [tris(hydroxymethyl)amino-methane], NaHCO<sub>3</sub>, KH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>.

- 15 Coloration a) is effected preferably at elevated temperature, for example at from 40 to 160°C. The temperature during coloration is especially from 60 to 140°C, more especially from 80 to 120°C. Coloration is then optionally followed by drying at from 40 to 160°C.

- The conversion of the colorant to its pigmentary form is then effected by conversion of the sulfonamide salt groups to sulfonamide groups. This is effected, unless the substrate to be pigmented is itself sufficiently acidic, by the addition of acid. Suitable acids are in principle any organic and inorganic acids. Preference is given to the use of organic C<sub>1-6</sub>-carboxylic acids, examples of which include formic acid, acetic acid, propionic acid, pivalic acid, oxalic acid, malonic acid, succinic acid and citric acid. The treatment with acid is preferably effected at room temperature. The concentration of the acid will be governed by the number of sulfonamide groups present in the salt form. Advantageously the acid is used in excess.
- 20
- 25

- The salts of sulfonamides according to the invention are suitable especially for the pigmenting of composite wood materials that are to be processed only after being coloured. Thin wooden panels through which the colorant has fully penetrated are stuck together and shaped and then cut at a wide variety of angles, yielding artistic effects as a result of the grain. Such materials can be used especially in the production of design articles or for decorative purposes. The demands in terms of fastness to light and penetration are substantially higher in this application than in customary wood veneers. Very homogeneous penetration of the individual wooden panels is especially important, even in the case of relatively large thicknesses, since the core thereof will be revealed by artistic cutting. Especially good results in that respect are obtained with compounds A1, B3 and
- 30
- 35

D12. Compound A1 in the full tone exhibits, after 20 hours' weathering, stability that is approximately 4 times greater than that of colorants C.I. Acid Red 194 and 361 and in the pastel tone, after 50 hours' weathering, exhibits a  $\Delta E^*$  that is twice as low as that of colorants C.I. Acid Red 194 and 361.

- 5 After 120 hours' weathering, in the full tone compound B3 exhibits a  $\Delta E^*$  that is approximately four times lower than C.I. Acid Red 194 and 361 and in the pastel tone, after 20 hours' weathering, exhibits a  $\Delta E^*$  that is approximately twice as low as that of C.I. Acid Red 194 and 361. Penetration into the wood matrix is good. A point of interest is the colour shift of some compounds after application. For example, compound A1 results in  
10 a red coloration, whereas compound B4 results in a brownish-red coloration and compound B5 results in an orange-red coloration.

- Compound D12 in the full tone, after 120 hours' weathering, exhibits a  $\Delta E^*$  that is approximately 3 to 4 times lower than that of C.I. Basic Blue 123 and C.I. Acid Blue 258 and, with the use of 10 % methoxypropanol as co-solvent, exhibits acceptable penetra-  
15 tion into the wood matrix. Special mention should be made in particular of the fastness to light of compound D12, which, after 600 hours' weathering, in the full tone exhibits a  $\Delta E^*$  of only 5. In the pastel tone compound D12, after 50 hours' weathering, exhibits a  $\Delta E^*$  that is approximately 3 to 4 times lower than that of C.I. Basic Blue 123 and C.I. Acid Blue 258.

- 20 The colorants according to the invention also yield very good results in inkjet printing. Compound D17 and compound D46 (2.5 % by weight-strength ink solutions) exhibit good printing results in printing using a bubble-jet printer and also a piezo printer; special mention should be made, in particular, of the very good water-resistance.

- Also in the pigmenting of anodised aluminium or alloys thereof, surprisingly, good results  
25 are obtained using the colorants according to the invention, that is to say in particular homogeneous coloration and very good fastness to light are obtained.

- Especially suitable as aluminium alloys are those wherein aluminium predominates, especially alloys with magnesium, silicon, zinc and/or copper, for example Al/Mg, Al/Si, Al/Mg/Si, Al/Zn/Mg, Al/Cu/Mg and Al/Zn/Mg/Cu, preferably those wherein the aluminium  
30 content is at least 90 % by weight; the magnesium content is preferably  $\leq 6$  % by weight; the silicon content is preferably  $\leq 6$  % by weight; the zinc content is preferably  $\leq 10$  % by weight and the copper content is advantageously  $\leq 2$  % by weight, especially  $\leq 0.2$  % by weight.

- The oxide layers formed on the metallic aluminium or on the aluminium alloys may have  
35 been produced by chemical oxidation or preferably galvanically by anodic oxidation. The

anodic oxidation of the aluminium or of the aluminium alloy for the passivation and formation of a porous layer can be effected according to known methods using direct current and/or alternating current, and using suitable electrolyte baths, for example with the addition of sulfuric acid, oxalic acid, chromic acid, citric acid or combinations of oxalic acid and chromic acid or sulfuric acid and oxalic acid. Such methods of anodisation are known in the art: DS method (direct current; sulfuric acid), DSX method (direct current; sulfuric acid with the addition of oxalic acid), DX method (direct current; oxalic acid), DX method with the addition of chromic acid, AX method (alternating current; oxalic acid), AX-DX method (oxalic acid; first alternating current and then direct current), AS method (alternating current; sulfuric acid) and chromic acid method (direct current; chromic acid). The current voltages are generally in the range from 5 to 80 Volt, preferably from 8 to 50 Volt; the temperatures are generally in the range from 5 to 50°C; the current density at the anode is generally in the range from 0.3 to 5 A/dm<sup>2</sup>, preferably from 0.5 to 4 A/dm<sup>2</sup>, in general current densities as low as  $\leq 2$  A/dm<sup>2</sup> being suitable for producing a porous oxide layer; at higher voltages and current densities, e.g. in the range from 100 to 150 Volt and  $\geq 2$  A/dm<sup>2</sup>, especially from 2 to 3 A/dm<sup>2</sup>, and at temperatures up to 80°C it is possible to produce especially hard and fine-pored oxide layers, for example according to the "Ematal" method using oxalic acid in the presence of titanium and zirconium salts. In the production of oxide layers that are then coloured adsorptively electrolytically or directly using a colorant of formula (I), in accordance with a preferred procedure that is customary *per se* in practice the current voltage is in the range from 12 to 20 Volt and the current density is preferably from 1 to 2 A/dm<sup>2</sup>. Such anodisation methods are generally known in the art and have also been described in detail in the specialist literature, e.g. in Ullmanns "Enzyklopädie der Technischen Chemie", 4th edition, volume 12, pages 196 to 198, or in the Sandoz brochures "Sanodal®" (Sandoz AG, Basle, Switzerland, Publication No. 9083.00.89) or in "Ratgeber für das Adsorptive Färben von Anodisiertem Aluminium" [Guide to the adsorptive colouring of anodised aluminium] (Sandoz, Publication No. 9122.00.80). The layer thickness of the porous oxide layer is advantageously in the range from 2 to 35 µm, preferably from 5 to 30 µm, especially from 15 to 25 µm.

In order to colour the oxide layer using the colorants of formula I or II, it is possible to use colouring methods that are customary *per se*, especially adsorption methods (substantially without current voltage), the colorant solution being applied to the surface of the oxide, for example, by spraying or roller application (depending on the form of the substrate) or preferably by immersion of the article to be coloured in a dye bath.

The coloration is effected advantageously at temperatures below the boiling point of the

liquor, advantageously at temperatures in the range from 15 to 80°C, preferably in the range from 15 to 70°C, especially from 20 to 60°C. The pH of the dye liquor is in the range from acidic to weakly basic, generally in the pH range from 3 to 8, preference being given to weakly acidic to virtually neutral conditions, especially a pH range of from 4 to 6. The colorant concentration and the duration of coloration can vary very widely depending upon the substrate and desired tinctorial effect. For example, colorant concentrations in the range of from 0.01 to 20 g/l, advantageously from 0.1 to 10 g/l, especially from 0.2 to 2 g/l, are suitable. The duration of coloration is generally in the range from 30 seconds to 1 hour and is preferably from 5 to 40 minutes.

The colorations obtained in that manner can be subjected to hot and/or cold sealing according to customary methods, optionally using suitable additives, the colorations advantageously being rinsed with water before sealing.

Sealing can be carried out in one or two steps, for example at pH values of from 4.5 to 8 using metal salts or oxides (e.g. nickel acetate or cobalt acetate) or using chromates.

Moreover, as described in DE-A-3327191, sealing can be carried out using organic sealing agents, for example organic phosphonates and diphosphonates or water-soluble (cyclo)aliphatic polycarboxylic acids or aromatic ortho-hydroxycarboxylic acids at pH values in the range from 4.5 to 8.

For cold sealing it is possible to use especially nickel or cobalt salts in combination with alkali metal fluorides, such as NaF. According to the invention, it is possible, e.g. as described in EP-A-1087038, to carry out cold sealing using a sealing agent containing nickel ions  $\text{Ni}^{2+}$  and fluoride ions  $\text{F}^-$ . Where appropriate, the sealing agents may comprise, for example, substrate- and/or coloration-stipulated sealing auxiliaries, for example cobalt compounds, in small amounts of up to 10 % by weight. The sealing agents can be used together with further adjuvants, such as (anionic) surfactants, especially sulfo-group-containing surfactants, preferably condensation products of sulfo-group-containing aromatic compounds with formaldehyde, for example condensation products of sulfonated naphthalene or/and sulfonated phenols with formaldehyde to form oligomeric condensation products having a surfactant character, and/or anti-smut agents (see e.g. DE-A-3900169 or DE-C-3327191), which contain, for example, salts of organic acids and non-ionic surfactants, for example P3-almeco seal® 1 (Henkel). The cold sealing is generally carried out at temperatures below 45°C, preferably in the range from 18 to 40°C, especially from 20 to 40°C. The  $\text{Ni}^{2+}$  concentration in the sealing bath is advantageously in the range from 0.05 to 10 g/l, preferably in the range from 0.1 to 5 g/l.

The pH value of the sealing bath is, for example, in the range from acidic to weakly basic, advantageously in the pH range from 4.5 to 8. The sealing time will depend on the

layer thickness and is, for example, from 0.4 to 2 minutes, preferably from 0.6 to 1.2 minutes, per  $\mu\text{m}$  thickness of the oxide layer of the substrate, sealing advantageously being carried out for from 5 to 60 minutes, preferably from 10 to 30 minutes. For the preferred oxide layers that are at least 15  $\mu\text{m}$  thick, preferably from 15 to 30  $\mu\text{m}$  thick, which are especially suitable for external architectural components, a sealing time of from 10 to 30 minutes is suitable.

Hot treatment with water is advantageously carried out in a temperature range of from 80°C to boiling temperature, preferably from 90 to 100°C, or also with steam at temperatures of from 95 to 150°C as appropriate under pressure, for example at an overpressure in the range of from 1 to 4 bar. The duration of after-sealing with water is generally in the range of from 15 to 60 minutes.

It may be advantageous to carry out two-step sealing, wherein in the first step cold sealing is carried out using at least one sealing agent, such as nickel acetate, optionally in the presence of a anti-smut agent, such as P3-almeco seal® 1 (Henkel), in deionised water, and in the second step hot after-sealing is carried out in deionised water.

In particular, two-step sealing is used in which in the first step cold sealing is carried out at about 40°C in deionised water using from 0.1 to 5 g/l, especially from 1.5 to 2.5 g/l, of nickel acetate in the presence of from 1 to 3 g/l of a anti-smut agent, such as P3-almeco seal® 1 (Henkel), for from 5 to 60 minutes, preferably from 10 to 30 minutes, and in the second step hot after-sealing is carried out in boiling, deionised water for from 15 to 60 minutes, especially from 30 to 45 minutes.

Treatment of the sealed aluminium substrates with a strongly inorganic acid, such as nitric acid, hydrochloric acid or phosphoric acid, can result in an increase in the fastness to light and/or a change in the colour of the pigmented aluminium substrates.

The colorants of formula I and/or II according to the invention are also suitable for colouring using plane-parallel flakes (effect pigments). Plane-parallel flakes are used as pigments in surface-coatings and printing inks and, in contrast to ground pigments, are distinguished by the fact that they can be made very thin. Since, after application of the surface-coating, they are oriented in such a manner that their plane surfaces extend parallel to the surface of the substrate, they produce (in contrast to ground pigments which reflect light more or less diffusely) a directed reflection of incident light.

A further embodiment of the present invention accordingly relates to coloured aluminium pigments that comprise platelet-shaped aluminium substrates coated with a metal oxide layer, the metal oxide layer comprising the pigments of formula I' and/or II' and the met-

als of the metal layer being selected from vanadium, titanium, zirconium, silicon, aluminium and boron.

The ratio of thickness to diameter of the flakes is referred to as the form factor and is generally from 1:50 to 1:500. Depending on the preparation process, the particle size distribution of the aluminium pigments is more or less statistical, having a  $d_{50}$  of from 5 to 50  $\mu\text{m}$ .

The amount of colorant is generally from 5 to 40 % by weight and the amount of metal oxide is from 3 to 95 % by weight, in each case based on the aluminium substrate.

The aluminium pigments can be obtained in analogy to a process described in DE-A-195 01 307, by producing the metal oxide layer by means of a sol-gel process by controlled hydrolysis of one or more metal acid esters in the presence of one or more of the colorants according to the invention, optionally in the presence of an organic solvent and optionally in the presence of a basic catalyst.

Suitable basic catalysts are, for example, amines, such as triethylamine, ethylenediamine, tributylamine, dimethylethanolamine and methoxypropylamine.

Suitable aluminium pigments are any customary aluminium pigments that can be used for decorative coatings and the oxidised coloured aluminium pigments described in DE-A-195 20 312. Preference is given to round aluminium flakes (so-called silver dollars).

The organic solvent is a water-miscible organic solvent, such as a  $C_{1-4}$ alcohol, especially isopropanol.

Suitable metal acid esters are selected from the group consisting of alkyl and aryl alcoholates, carboxylates and carboxyl-, alkyl- or aryl-substituted alkyl alcoholates or carboxylates of vanadium, titanium, zirconium, silicon, aluminium and boron. Preference is given to the use of triisopropyl aluminate, tetraisopropyl titanate, tetraisopropyl zirconate, tetraethyl orthosilicate and triethyl borate. It is also possible to use acetylacetonates and acetoacetylacetonates of the above-mentioned metals. Preferred examples of that kind of metal acid ester are zirconium, aluminium and titanium acetylacetonate and diisobutyleyl acetoacetylaluminate or diisopropyleyl acetoacetylacetonate and mixtures of metal acid esters, for example Dynasil® (made by Hüls); a mixed aluminium-silicon metal acid ester.

Moreover, the aluminium pigment can be prepared analogously to a process described in EP-A-0 380 073. A layer of an anodically oxidisable metal is applied to a carrier that has optionally been coated with a separating agent, which layer has a thickness corresponding to at least 500 nm and which is oxidised anodically in an electrolyte at a voltage of from 0.5 to 100 V. The porous metal oxide layer is then coloured using the color-



ants according to the invention and sealed. The separating agent is then dissolved in a suitable solvent, the aluminium pigment precipitating in the form of coarse flakes which can be further processed by separation of the solvent, drying and milling (see, for example, WO01/25500 A1).

- 5 The carrier that has been coated with an anodically oxidisable metal can be obtained according to known processes. It is advantageous to use carriers to which a thin metal layer has been applied by sputtering or by chemical methods or by vapour-deposition *in vacuo*. The layer thickness of the metal is advantageously so selected that the metal layer remaining after anodic oxidation is covered with a metal oxide layer of a thickness  
10 of at least 10 nm, preferably at least 100 nm. The layer thickness of the metal is generally from 500 nm to 5 µm, preferably from 1 µm to 2 µm.

- Suitable electrolytes are known and are described, for example, in J. Elektrochem. Soc.: Electrochemical Science and Technology, 122,1, p. 32 (1975). There are suitable, for example, dilute aqueous solutions (e.g. up to 20 % by weight) of inorganic acids or of  
15 carboxylic acids (sulfuric acid, phosphoric acid, chromic acid, formic acid, oxalic acid), of alkali metal salts of inorganic acids or of carboxylic acids (sodium sulfate, sodium bisulfate, sodium formate), and alkali metal hydroxides (KOH, NaOH).

- The anodic oxidation can be carried out at a temperature of from 0 to 60°C and preferably at room temperature. The voltage to be selected will depend substantially on the  
20 electrolyte used and is generally from 0.5 to 100 V. Electrolysis can be carried out using alternating current or preferably using direct current.

- The carrier has a surface of metal, glass, enamel, ceramics or an organic material and can be of any desired shape, foils, films and plates being preferred. The carrier can be, for example, a glass, a mineral (quartz, sapphire, ruby, beryl or silicate), a ceramic mate-  
25 rial, silicon or a synthetic material (cellulose, polymethacrylate, polycarbonate, polyester, polyolefin, polystyrene).

- The separating agent will be an inorganic separating agent, such as a separating agent that can be evaporated *in vacuo*, such as a chloride, borate, fluoride or hydroxide, or some other inorganic substance described, for example, in US-A-5 156 720 and  
30 US-A-3 123 489, or an organic separating agent, such as a surface-coating, sodium stearate, lithium stearate, magnesium stearate, aluminium stearate, a fatty alcohol or a wax alcohol of the type  $C_xH_yO$  wherein  $15 < C < 30$ , a paraffin wax, a branched or unbranched fatty acid wherein  $C > 15$  or a thermoplastic polymer.

- The metal layer is formed of aluminium itself or of an aluminium alloy with, for example,  
35 Mg or Zn. A preferred lower limit for the layer thickness is 500 nm. The upper limit for

the layer thickness is a maximum of 5.0  $\mu\text{m}$ . The thickness is preferably from 0.5 to 3.0  $\mu\text{m}$  and especially from 1.0 to 2.0  $\mu\text{m}$ .

The thickness of the oxide layer will depend substantially on the initial thickness of the metal layer. The oxide layer can be, for example, from 10 nm to 500 nm. Preferred layer thickness ranges are from 100 nm to 500 nm.

The diameter of the pores in the metal oxide layer will depend substantially on the preparation conditions during electrolysis; especially on the electrolyte used. The diameter can be, for example, from 2 nm to 500 nm.

The aluminium pigments according to the invention can be used to provide a special effect in paints, coatings, plastics, printing inks and cosmetic preparations.

The following Examples illustrate the invention.

### Examples

#### Synthesis Example 1: Synthesis of compound A1

##### Sulfochlorination:

230 g of chlorosulfonic acid are placed in a 0.5 litre round-bottomed flask which is provided with a stirrer, thermometer and condenser. 45 g of C.I. Pigment Red 264 (0.1 mol) are introduced, in portions, at room temperature. The resulting solution is heated slowly to 140°C and stirred for 4 hours. The solution is cooled and 85 g of thionyl chloride are slowly added dropwise at 75°C. Stirring is then carried out for a further 4 hours at reflux. At room temperature, the solution is poured onto 2.5 kg of ice, and the resulting suspension is filtered and washed thoroughly with water.

##### Amination:

122 g of ethanolamine (2 mol) are placed in a 1 litre round-bottomed flask and cooled to 0°C by the addition of ice. The moist aqueous filter cake is introduced in portions, the temperature being maintained at 0°C by the further addition of ice. The suspension is stirred for one hour at 0°C, for 14 hours at room temperature and for 1 hour at 80°C.

The suspension is cooled and 350 g of 32 % hydrochloric acid solution are added dropwise. At room temperature, the suspension is filtered and washed with 3 % hydrochloric acid solution. Drying *in vacuo* at 80°C yields 70 g of compound A1.

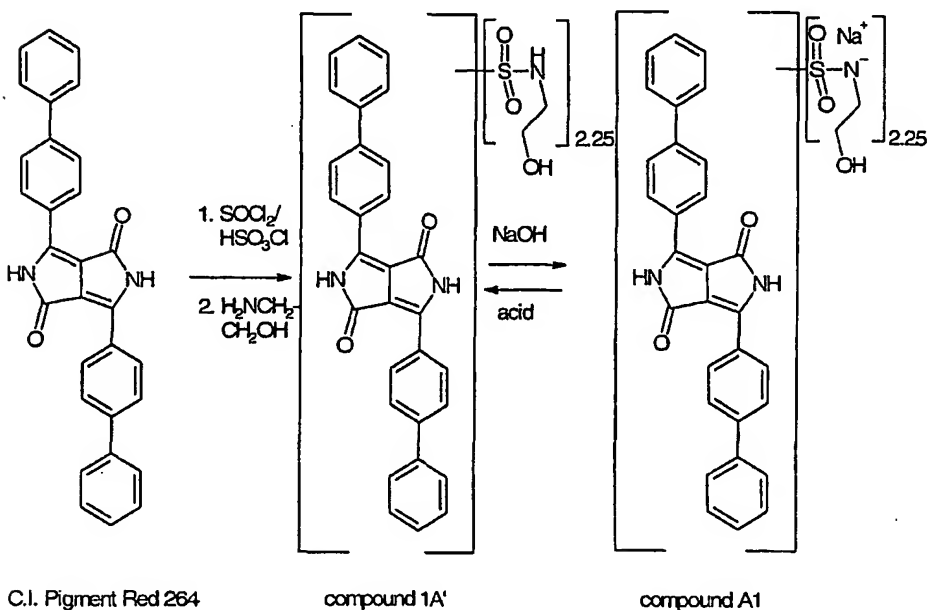
The  $^1\text{H}$ -NMR shows that compound A1 is both a mixture of structural isomers and a mixture of two- to three-fold sulfochlorinated and amidated molecules (ratio: 25% three-fold, 75% twofold sulfochlorinated species).

Elemental analysis (theory): C: 57.33% (57.94%), H: 4.18% (4.36%), N: 7.65% (8.28%), S: 10.32% (9.98%).

Conversion of compound A1' into compound A1

20 g of compound A1' are suspended in 200 g of water in a 1 litre round-bottomed flask. At room temperature, 7.5 g of 30% sodium hydroxide solution are added dropwise. The resulting solution is stirred for 2 hours at 60°C and filtered while warm, and the filtrate is concentrated by evaporation at a maximum of 80°C and at reduced pressure. Drying *in vacuo* at 80°C yields 21 g of compound A1.

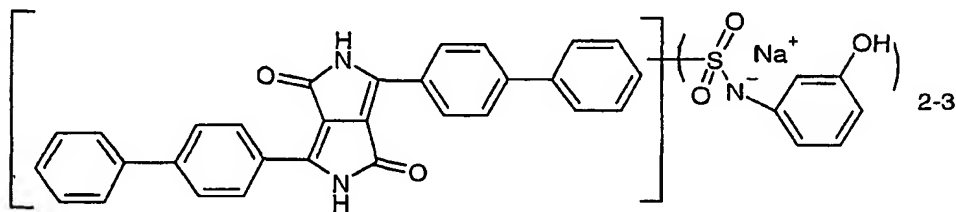
Elemental analysis, based on a 1:3 mixture of twofold and threefold sulfochlorinated molecules (theory): C: 53.33% (54.10%), H: 3.78% (4.10%), N: 7.15% (7.73%), S: 9.72% (9.30%), Na: 6.98 % (6.67 %).



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**Synthesis Example 2: Synthesis of compound A2**

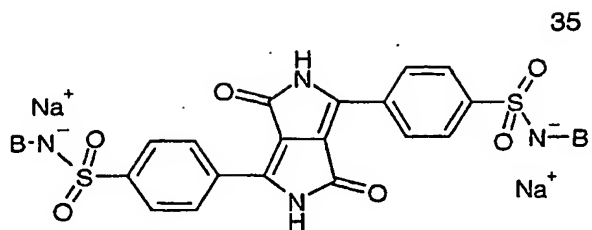
Compound A2 is prepared analogously to Synthesis Example 1.



15

compound A2

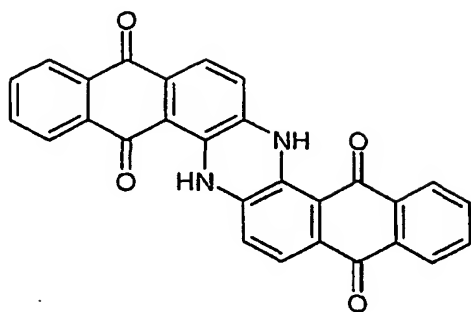
Compounds B1 to B5 are prepared analogously to Synthesis Example 1.



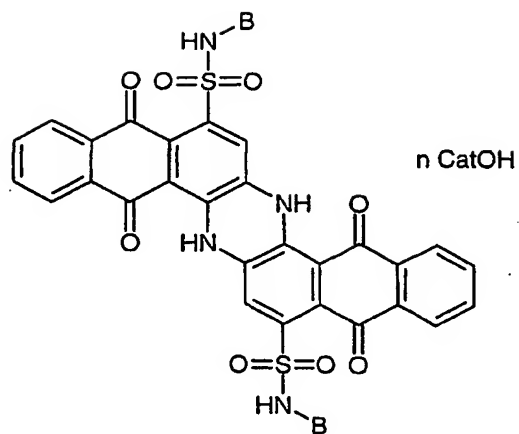
Synthesis Example	Compound	B
3	B1	
4	B2	
5	B3	
6	B4	
7	B5	

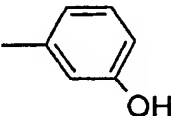
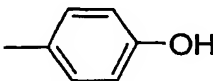
5 **Synthesis Examples 8 to 15: Synthesis of compounds C1 to C8**

Compounds C1 to C8 are prepared analogously to Synthesis Example 1 starting from C.I. Pigment Blue 60.



C.I. Pigment Blue 60



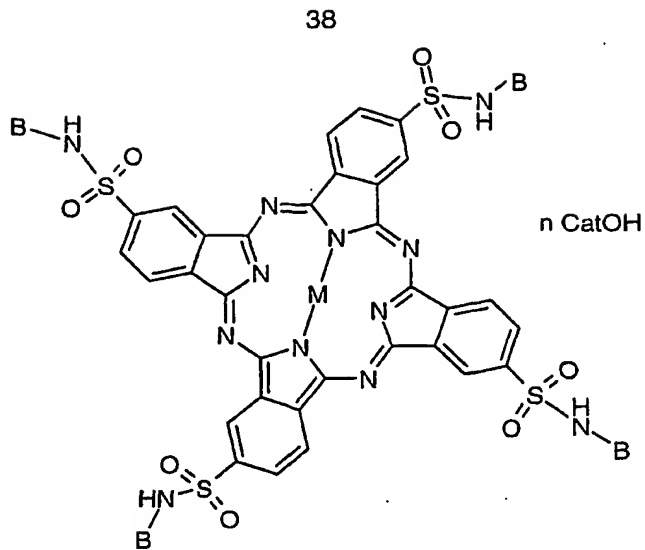
Synthesis Example	Compound	B	n Cat
8	C1	-CH <sub>2</sub> CH <sub>2</sub> OH	2 Na <sup>+</sup>
9	C2		2 Na <sup>+</sup>
10	C3	.	4 Na <sup>+</sup>
11	C4	H	Na <sup>+</sup>
12	C5	H	2 Na <sup>+</sup>
13	C6		Na <sup>+</sup>
14	C7	.	2 Na <sup>+</sup>
15	C8	.	3 Na <sup>+</sup>

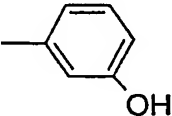
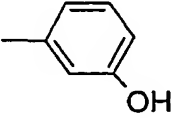
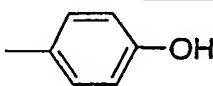
**Synthesis Example 17: Synthesis of compound D1**

10 g of compound D1' (for preparation, see Example 1 of WO 98/45756) are suspended  
 5 in 150 g of water in a 500 ml round-bottomed flask. At room temperature, 5.4 g of  
 30 % sodium hydroxide solution are added dropwise. The resulting solution is stirred at  
 60°C for 3 hours and filtered while warm, and the filtrate is concentrated at a maximum  
 of 80°C and at reduced pressure using a rotary evaporator. Drying *in vacuo* at 80°C  
 yields 21 g of compound D1.

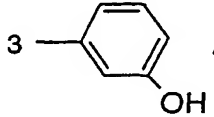
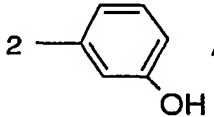
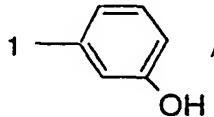
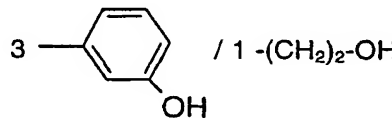
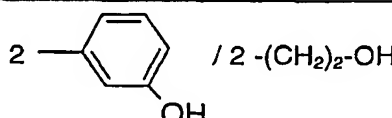
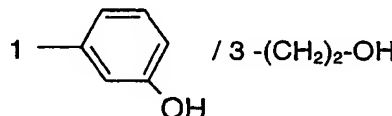
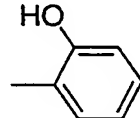
10 Elemental analysis (theory): C: 41.37% (41.54%), H: 2.96% (2.79%), N: 14.14%  
 (14.53%), Cu 5.36 (5.49%) Na 8.26% (7.95%), S 10.91% (11.09%).

Compounds D2 to D55 are prepared analogously to Synthesis Example 17.

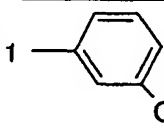
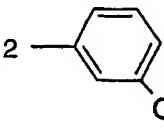
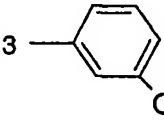
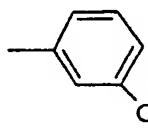

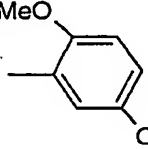
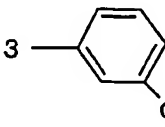


Synthesis Example	Compound	B	M	n Cat
17	D1	$-(CH_2)_2-OH$	Cu	4 Na <sup>+</sup>
18	D2	$-(CH_2)_2-OH$	Cu	6 Na <sup>+</sup>
19	D3	$-(CH_2)_2-OH$	Cu	8 Na <sup>+</sup>
20	D4	$-(CH_2)_2-OH$	Cu	4 Li <sup>+</sup>
21	D5	$-(CH_2)_2-OH$	Cu	8 Li <sup>+</sup>
22	D6	$-(CH_2)_2-OH$	Cu	4 N(CH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>
23	D7		Cu	4 Na <sup>+</sup>
24	D8	"	Cu	8 Na <sup>+</sup>
25	D9		Cu	4 N(CH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>
26	D10	"	Cu	8 N(CH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>
27	D11		Cu	4 Na <sup>+</sup>
28	D12	"	Cu	8 Na <sup>+</sup>

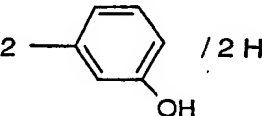
39

29	D13	 / 1 H	Cu	7 Na <sup>+</sup>
30	D14	 / 2 H	Cu	3 Na <sup>+</sup>
31	D15	"	Cu	4 Na <sup>+</sup>
32	D16	"	Cu	6 Na <sup>+</sup>
33	D17	 / 3 H	Cu	3 Na <sup>+</sup>
34	D18	"	Cu	4 Na <sup>+</sup>
35	D19	"	Cu	5 Na <sup>+</sup>
36	D20	 / 1 -(CH <sub>2</sub> ) <sub>2</sub> -OH	Cu	6 Na <sup>+</sup>
37	D21	"	Cu	8 Na <sup>+</sup>
38	D22	 / 2 -(CH <sub>2</sub> ) <sub>2</sub> -OH	Cu	6 Na <sup>+</sup>
39	D23	"	Cu	8 Na <sup>+</sup>
40	D24	 / 3 -(CH <sub>2</sub> ) <sub>2</sub> -OH	Cu	4 Na <sup>+</sup>
41	D25	"	Cu	6 Na <sup>+</sup>
42	D26	"	Cu	8 Na <sup>+</sup>
43	D27		Cu	3 Na <sup>+</sup>
44	D28	"	Cu	4 Na <sup>+</sup>
45	D29	"	Cu	6 Na <sup>+</sup>
46	D30	"	Cu	8 Na <sup>+</sup>
47	D31	-(CH <sub>2</sub> ) <sub>3</sub> -OH	Cu	4 Na <sup>+</sup>



48	D32	$-(\text{CH}_2)_3\text{-OH}$	Cu	6 Na <sup>+</sup>
49	D33	$-(\text{CH}_2)_3\text{-OH}$	Cu	8 Na <sup>+</sup>
50	D34	 $/3 -(\text{CH}_2)_3\text{-OCH}_3$	Cu	4 Na <sup>+</sup>
51	D35	"	Cu	5 Na <sup>+</sup>
52	D36	 $/2 -(\text{CH}_2)_3\text{-OCH}_3$	Cu	5 Na <sup>+</sup>
53	D37	"	Cu	6 Na <sup>+</sup>
54	D38	 $/1 -(\text{CH}_2)_3\text{-OCH}_3$	Cu	6 Na <sup>+</sup>
55	D39	"	Cu	7 Na <sup>+</sup>
56	D40	$-(\text{CH}_2)_2\text{-OH}$	Zn	4 Na <sup>+</sup>
57	D41	$-(\text{CH}_2)_2\text{-OH}$	Zn	8 Na <sup>+</sup>
58	D42		Zn	8 Na <sup>+</sup>
59	D43		Zn	4 Na <sup>+</sup>
60	D44	.	Zn	8 Na <sup>+</sup>
61	D45		Zn	8 Na <sup>+</sup>
62	D46	H	Zn	2 Na <sup>+</sup>
63	D47	H	Zn	3 Na <sup>+</sup>
64	D48	H	Zn	4 Na <sup>+</sup>
65	D49	 $/1 \text{ H}$	Zn	4 Na <sup>+</sup>
66	D50	.	Zn	7 Na <sup>+</sup>

41

67	D51	 / 2 H	Zn	4 Na <sup>+</sup>
68	D52	.	Zn	6 Na <sup>+</sup>
69	D53	-(CH <sub>2</sub> ) <sub>2</sub> OH	Cu	8 NH <sub>4</sub> <sup>+</sup>
70	D54	H	Cu	1 Na <sup>+</sup>
71	D55	2 -(CH <sub>2</sub> ) <sub>2</sub> OH/2 H	Cu	1 Na <sup>+</sup>

**Synthesis Example 33: Synthesis of compound D17**

In a 750 ml sulfonating flask, 2.03 g of 3-aminophenol (0.026 mol) and 5.31 g of a 25 % ammonium hydroxide solution (0.078 mol) are introduced into a mixture of 9.4 g of water and 16.6 g of methanol and cooled to 0°C by the addition of ice. 0.026 mol of copper phthalocyaninetetrasulfonic acid chloride is introduced in portions, the temperature being maintained at 0°C by further addition of ice. The suspension is stirred for 30 minutes at 0°C and for 14 hours at room temperature. The suspension is cooled and 10 g of 32 % hydrochloric acid solution are added dropwise. At room temperature, the suspension is filtered and washed with 3 % hydrochloric acid solution. Drying *in vacuo* at 70°C yields 23.7 g of the sulfonamide D8'.

2 g of D8' are suspended in 200 g of water in a 500 ml round-bottomed flask. 0.8 g of 30% sodium hydroxide solution is added dropwise at room temperature. The resulting solution is stirred at 60°C for 2 hours and filtered while warm, and the filtrate is concentrated by evaporation at a maximum of 80°C and at reduced pressure. Drying *in vacuo* at 80°C yields 2.1 g of compound D17, which exhibits a pH value of 7.

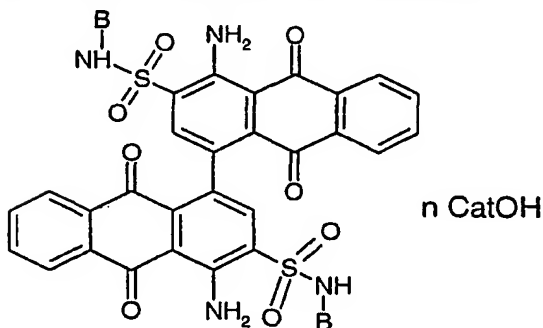
**Synthesis Example 62: Synthesis of compound D46**

Compound D46 is prepared analogously to Synthesis Example 17. Two equivalents of sodium hydroxide are used to form the salt in the last step. Only some of the amide functions are converted to a salt in order to establish a suitable pH value for the pigmenting of aluminium (see Application Example 7).

**Synthesis Example 72: Synthesis of compound E1**

44.8 g of chlorosulfonic acid are introduced into a 250 ml sulfonating flask that is provided with a stirrer, thermometer and condenser. 10.0 g of 4,4'-diamino-1,1'-bisanthraquinone-3,3'-disodium sulfonate (0.0154 mol) are added in portions at room temperature. The resulting red solution is heated slowly to 40°C and 13.2 g of thionyl

- chloride (0.11 mol) are added dropwise with stirring. The mixture is then heated to 70°C and maintained at that temperature for 2 hours. After the solution has cooled, it is poured into a mixture of 50 g of water and 190 g of ice and the resulting suspension is filtered and washed thoroughly with water. The moist filter cake is added in portions, at 0°C, to a solution of 5.0 g of 3-aminophenol in a mixture of 8 g of water and 27 g of methanol. The suspension is stirred for one hour at 0°C, for 14 hours at room temperature and for 1 hour at 80°C. The suspension is cooled and 6 g of 32 % hydrochloric acid solution are added dropwise. At room temperature, the suspension is filtered and washed with 3 % hydrochloric acid solution. Drying *in vacuo* at 80°C yields 10 g of the disulfonamide E1'.
- 2 g of the disulfonamide E1' are suspended in 100 g of water in a 250 ml round-bottomed flask. At room temperature, 0.67 g of 30% sodium hydroxide solution are added dropwise. The resulting solution is stirred at 60°C for 2 hours and filtered while warm, and the filtrate is concentrated by evaporation at a maximum of 80°C and under reduced pressure. Drying *in vacuo* at 80°C yields 1.87 g of E1.
- Elemental analysis (theory): C: 57.66% (57.83%), H: 3.29% (2.91%), N: 6.55% (6.74%), S: 7.73% (7.72%), Na: 5.97% (5.53%).

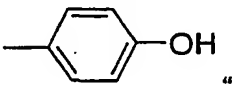


Compounds E2 to E8 are synthesised analogously to Synthesis Example 72.

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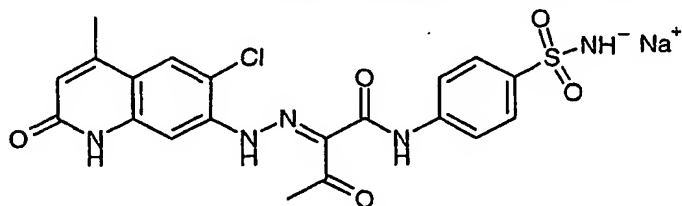
Synthesis Example	Compound	B	n Cat
72	E1		2 Na <sup>+</sup>
73	E2	"	1 Na <sup>+</sup>
74	E3	"	3 Na <sup>+</sup>
75	E4	-(CH <sub>2</sub> ) <sub>2</sub> -OH	1 Na <sup>+</sup>

43

76	E5	$-(CH_2)_2-OH$	$2 Na^+$
77	E6	H	$1 Na^+$
78	E7	H	$2 Na^+$
79	E8		$2 Na^+$

**Synthesis Example 80: Synthesis of F1**

Compound F1 is obtained analogously to Synthesis Example 62.

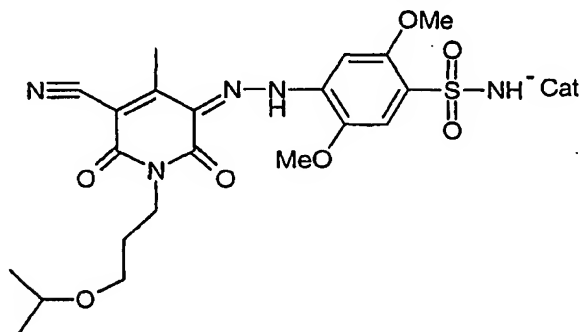


Compound F1

5

**Synthesis Examples 81 to 83: Synthesis of G1 to G3**

Compounds G1 to G3 are obtained analogously to Synthesis Example 62.



Compound G1

Synthesis Example	Compound	B	Cat
81	G1	H	$NH_4^+$
82	G2	H	$HO(CH_2)_2NH_3^+$
83	G3	H	$Na^+$

10

**Full tone coloration:**

For full tone coloration, a 0.5-2 % solution is used. The application time is 6 hours at  $110^\circ C$  in an autoclave. Thereafter, the wood is dried for 30 minutes at  $80^\circ C$ , immersed

in 5% citric acid at room temperature for 1 hour and finally dried at 130°C for 30 minutes.

**Pastel tone coloration:**

- 5 For pastel tone coloration, a 0.05-0.2 % solution is used. The application time is 6 hours at 110°C in an autoclave. Thereafter, the wood is dried for 30 minutes at 80°C, immersed in 5% citric acid at room temperature for 1 hour and finally dried at 130°C for 30 minutes.

10 **Exposure test in a weathering device (ATLAS WOM 6500W xenon radiation device):**

The coloured samples are mounted on frames (width 44 or 60 mm) and irradiated for up to 600 hours in the weathering device under the following parameters:

-filter system: quartz internal filter/borosilicate external filter, corresponding to:

- 15       0.35 W/m<sup>2</sup> at 340 nm or 0.126 J/cm<sup>2</sup>/h  
          from 340 to 420 nm: 17-18 J/cm<sup>2</sup>/h  
          from 340 to 700 nm: 122-125 J/cm<sup>2</sup>/h

-black-panel temperature: 63°C

-rel. humidity: 60%

- 20 Lightness (L), saturation (C) and hue (h) are measured using a spectrophotometer before irradiation and after 25, 50, 120, 240, 360, 480 and 600 hours' exposure. The corresponding colour differences and overall colour difference  $\Delta E^*$  are calculated therefrom.

25 **Application Example 1: Pigmenting of wood**

- 1 to 5 pieces of dark obeche wood (115x30x1mm) are immersed, in a sealed container (L = 130mm, diameter 36 mm), in a solution of 1.0 % compound A1 + 0.15 % NaHCO<sub>3</sub> + 0.1 % Invadin in deionised water and are coloured at 110°C for 6 hours with continuous rotation. 15 minutes' drying at 100°C yields pieces of dark-red wood exhibiting homogeneous penetration, which are immersed for 1 hour in 5 % citric acid + 0.5 % Invadin in water and then dried for five minutes at 160°C.
- 30

**Application Example 2: Pigmenting of wood**

- 1 to 5 pieces of bleached obeche wood are immersed and coloured thoroughly, analogously to Application Example 1, for 6 hours at 110°C in a solution of 0.05% compound
- 35

A1 + 0.1%  $\text{NaHCO}_3$  + 0.1% Invadin in deionised water. Drying for fifteen minutes at 100°C yields pieces of light-red wood exhibiting homogeneous penetration.

### Application Example 3: Pigmenting of wood

5 1 to 5 pieces of dark obeche wood (115x30x1mm) are immersed and coloured thoroughly, analogously to Application Example 1, for 6 hours at 110°C in a solution of 0.55 % compound D1 + 0.15 %  $\text{NaHCO}_3$  + 0.1 % Invadin in deionised water. Drying for fifteen minutes at 100°C yields pieces of dark-blue wood exhibiting good penetration, which are immersed for 1 hour in 5 % citric acid + 0.5 % Invadin in water and then dried for  
10 5 minutes at 160°C. The colorant is insoluble in water after the treatment (no bleeding).

### Application Example 4: Pigmenting of wood

1 to 5 pieces of dark obeche wood (115x30x1mm) are immersed and coloured thoroughly, analogously to Application Example 1, for 6 hours at 110°C in a solution of 0.5%  
15 compound F4 + 0.35 %  $\text{Na}_2\text{CO}_3$  + 0.1 % Invadin in warm deionised water. Drying for fifteen minutes at 100°C yields pieces of yellow wood exhibiting homogeneous penetration, which are immersed for 1 hour in 5 % citric acid + 0.5 % Invadin in water and then dried for five minutes at 160°C. The colorant is insoluble in water after the treatment (no bleeding).

20

### Application Example 5: Inkjet printing

Compound D9 (4 equivalents of tetramethylammonium hydroxide) and compound D10 (8 equivalents of tetramethylammomium hydroxide) are tested in inks (2.5 % by weight strength solutions). They exhibit good printing results in printing using a bubble-jet  
25 printer and using a piezo printer. The chromaticity and the colour hue are within a range to be expected on the basis of the chromaticity and colour hue of the compounds not substituted by sulfonamide groups. The water-resistance is very good.

### Application Example 6: Pigmenting of wood

30 1 to 5 pieces of dark obeche wood (115x30x1mm) are immersed and coloured thoroughly, analogously to Application Example 1, for 6 hours at 110°C in a solution of 0.05% compound E1 + 0.15 %  $\text{Na}_2\text{CO}_3$  + 0.1 % Invadin in warm deionised water. Drying for fifteen minutes at 100°C yields pieces of yellow wood exhibiting homogeneous penetration, which are immersed for 1 hour in 5 % citric acid + 0.5 % Invadin in water  
35 and then dried for five minutes at 160°C. The colorant is insoluble in water after the

then dried for five minutes at 160°C. The colorant is insoluble in water after the treatment (no bleeding).

#### **Application Example 7: Pigmenting of anodised aluminium**

- 5 A degreased and deoxidised sheet of pure aluminium is oxidised anodically in an aqueous solution containing, in 100 parts, from 18 to 22 parts of sulfuric acid and from 1.2 to 7.5 parts of aluminium sulfate, at a temperature of from 18 to 20°C, at a voltage of from 15 to 16 Volt with direct current of a density of 1.5 A/dm<sup>2</sup>, for from 30 to 40 minutes. An oxide layer of about from 18 to 20 µm thickness is formed having a porosity of 17%.
- 10 After rinsing with water, the anodised aluminium sheet is coloured for 40 minutes at 60°C in a solution consisting of 0.5 part of colorant D-54 in 100 parts of deionised water, the pH of which has been adjusted to 5.5 with acetic acid and sodium acetate. The alox layer is then sealed for 20 minutes at 40°C in a solution of 2 g/litre of nickel acetate and 2 g/litre of P3-almeco seal® (Henkel) in deionised water and then sealed again for
- 15 40 minutes in boiling deionised water. The sample is then exposed in an Atlas-Weather-O-meter Ci 65 A. The colour difference  $\Delta E$  resulting after 1500 hours is 5.0. Similar results are obtained with colorant D-55.

- Compound A1 is tested in respect of full tone coloration and pastel tone coloration. The
- 20 penetration is measured and the light stability is compared with the light stability of the standard dyes C.I. Acid Red 194 and 361. Compound A1 exhibits very good penetration and no bleeding. If the acid treatment is omitted during pigmenting with compound A1, the obeche veneers obtained in that manner exhibit a slight degree of bleeding. After 20 hours' weathering, compound A1 exhibits stability that is about 4 times greater than
- 25 that of dyes C.I. Acid Red 194 and 361. Compound A1 not treated with acid exhibits slightly less stability. In the pastel tone, after 50 hours' weathering, compound A1 exhibits a  $\Delta E^*$  that is twice as low as that of dyes C.I. Acid Red 194 and 361.

- Compounds B2 and B3 are tested in the full tone and in the pastel tone in comparison with standard dyes C.I. Acid Red 194 and 361. After 120 hours' weathering, compound
- 30 B2 exhibits in the full tone a  $\Delta E^*$  that is approximately twice as low, and compound B3 exhibits a  $\Delta E^*$  that is approximately 4 times as low, as C.I. Acid Red 194 and 361. In the pastel tone, after 20 hours' weathering both compound B2 and B3 exhibit a  $\Delta E^*$  that is approximately twice as low as C.I. Acid Red 194 and 361. The penetration into the wood matrix is good for both compounds B2 and B3. A point of interest is the colour shift of
- 35 some compounds after application. Compound A1 results in a red coloration, whereas

compound B4 results in a brownish-red coloration and compound B5 results in an orange-red coloration.

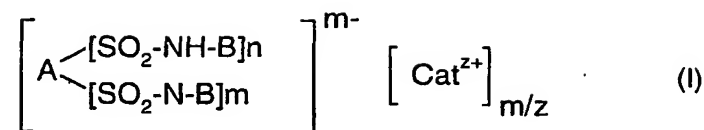
The fastness to light of compounds D1, D8, D12 and D40 is compared in the full tone and in the pastel tone with the standard dyes C.I. Basic Blue 123 and C.I. Acid Blue 258.

- 5 The copper phthalocyanine derivatives, compounds D8 and D12 in the full tone, after 120 hours' weathering, exhibit a  $\Delta E^*$  that is approximately 3 to 4 times lower than that of C.I. Basic Blue 123 and C.I. Acid Blue 258 and, using 10 % methoxypropanol as co-solvent, exhibit acceptable penetration into the wood matrix. Special mention may be made, in particular, of the fastness to light of compound D8, which, after 600 hours' weathering, in the full tone exhibits a  $\Delta E^*$  of only 5. In the pastel tone compounds D8 and D12, after 50 hours' weathering, exhibit a  $\Delta E^*$  that is approximately 3 to 4 times lower than that of C.I. Basic Blue 123 and C.I. Acid Blue 258. The zinc phthalocyanine derivative (compound D40) is, in respect of fastness to light, slightly better than C.I. Basic Blue 123 and C.I. Acid Blue 258 and exhibits better penetration into the wood matrix than the copper phthalocyanine derivatives.
- 10
- 15

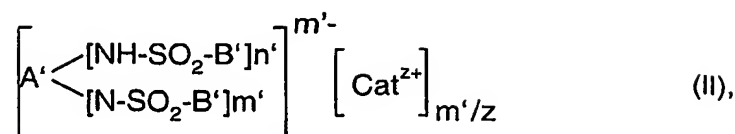


What is claimed is:

1. A colorant of the general formula



or



wherein n and n' denote a value from 0 to 4,

m and m' denote a value from 1 to 8, the sum of m + n and of m' and n' being less than or equal to 8,

z is an integer from 1 to 5, especially 1,

A is the radical of a chromophore of the series 1-aminoanthraquinone, anthraquinone, anthrapyrimidine, azo, azomethine, benzodifuranone, quinacridone, quinacridonequinone, quinophthalone, diketopyrrolopyrrole, dioxazine, flavanthrone, indanthrone, indigo, isoindoline, isoindolinone, isoviolanthrone, perinone, perylene, phthalocyanine, pyranthrene or thioindigo,

A' is the radical of a chromophore that already contains one or more primary amino groups, such as 1-aminoanthraquinone, or A' is one of the chromophore radicals listed under A modified with from 1 to 8, preferably with from 1 to 4, amino groups,

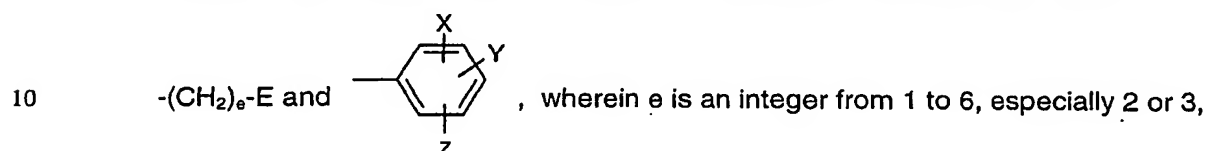
Cat is an alkali metal cation or an ammonium cation and

B and B' are each independently of the other a branched or straight-chain C<sub>1-8</sub>-alkyl, C<sub>2-8</sub>alkenyl, C<sub>2-8</sub>alkynyl, aryl, N-, O- or S-containing 5- or 6-membered heterocyclic ring, C<sub>1-8</sub>alkylarylene, aryl-C<sub>1-8</sub>alkylene or aryl-L-arylene radical, which may be substituted by one or more groups -OH, -OCat, -SH, -SCat, -OR<sup>1</sup>, -SR<sup>2</sup>, -C(O)OR<sup>3</sup>, -C(O)R<sup>4</sup> and/or -NR<sup>5</sup>R<sup>6</sup>, it being possible for the C<sub>1-8</sub>alkyl radical to be uninterrupted or interrupted one or more times by -O- or by -S-,

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are each independently of the others a C<sub>1-8</sub>alkyl radical, a C<sub>7-11</sub>-

aralkyl radical or a  $C_{6-12}$ aryl radical and  $R^4$  can additionally be a hydrogen atom, L is a bond'  $-NR^7$ , wherein  $R^7$  is a hydrogen atom or a  $C_{1-4}$ alkyl radical, or an  $-N=N-$  group, and  $R^5$  and  $R^6$  are each independently of the other a hydrogen atom, a  $C_{1-8}$ alkyl radical, a  $C_{1-4}$ alkoxy- $C_{1-4}$ alkyl radical, a  $C_{6-12}$ aryl radical, a  $C_{7-11}$ aralkyl radical or a radical  $-(CH_2)_oOH$ , wherein o is an integer from 2 to 6, and B can additionally be a hydrogen atom, it being possible for B and B' within a chromophore A or A' to have different substituent meanings.

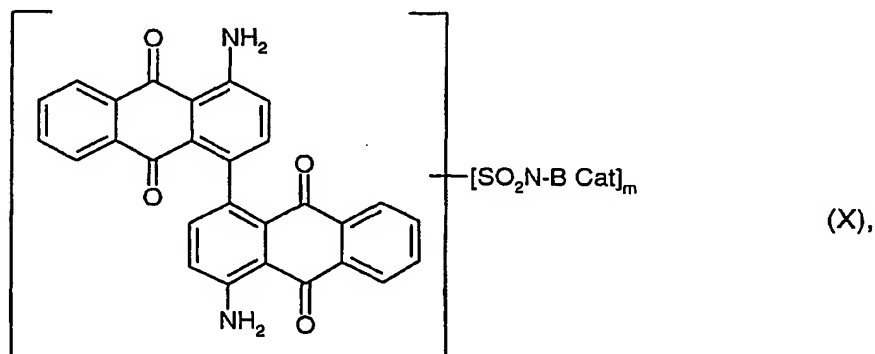
2. A colorant according to claim 1, wherein B is selected from a hydrogen atom,



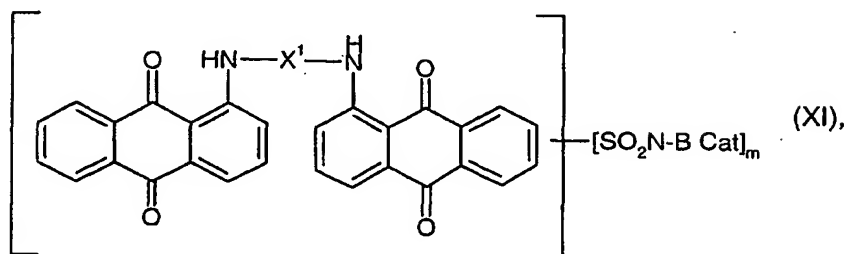
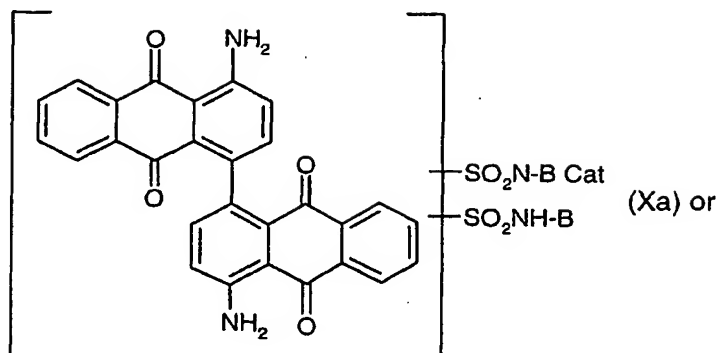
E is a hydrogen atom, a group  $-OH$ ,  $-OCat$ ,  $-SH$ ,  $-SCat$ ,  $-OR^1$ ,  $-SR^2$ ,  $-NR^5R^6$  or  $-C(O)OR^3$ , and X, Y and Z are each independently of the others selected from a hydrogen atom and a group  $-OH$ ,  $-OCat$ ,  $-SH$ ,  $-SCat$ ,  $-OR^1$ ,  $-SR^2$ ,  $-NR^5R^6$  and  $-C(O)OR^3$ , wherein  $R^1$ ,  $R^2$  and  $R^3$  are each independently of the others a  $C_{1-4}$ alkyl radical, especially methyl or ethyl, and  $R^5$  and  $R^6$  denote a radical  $-(CH_2)_oOH$ , wherein o is an integer from 2 to 6, and Cat is a sodium or potassium cation, unsubstituted ammonium or an ammonium cation.

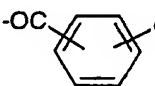
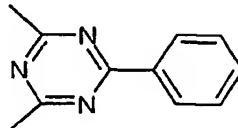
3. A colorant according to claim 1 or 2, wherein n is 0.

4. A colorant according to any one of claims 1 to 3, namely  
- a 1-aminoanthraquinone or anthraquinone derivative of formula



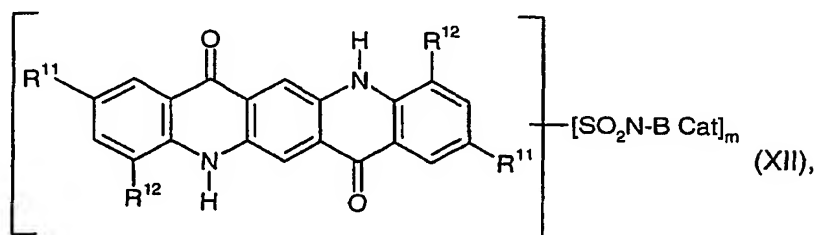
- 50 -



wherein X<sup>1</sup> is a group  or  and m denotes a va-

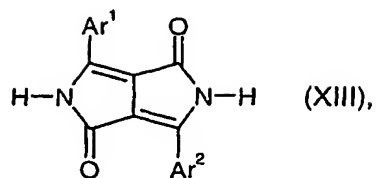
lue from 1 to 4, especially from 2 to 3;

5 - a quinacridone derivative of formula

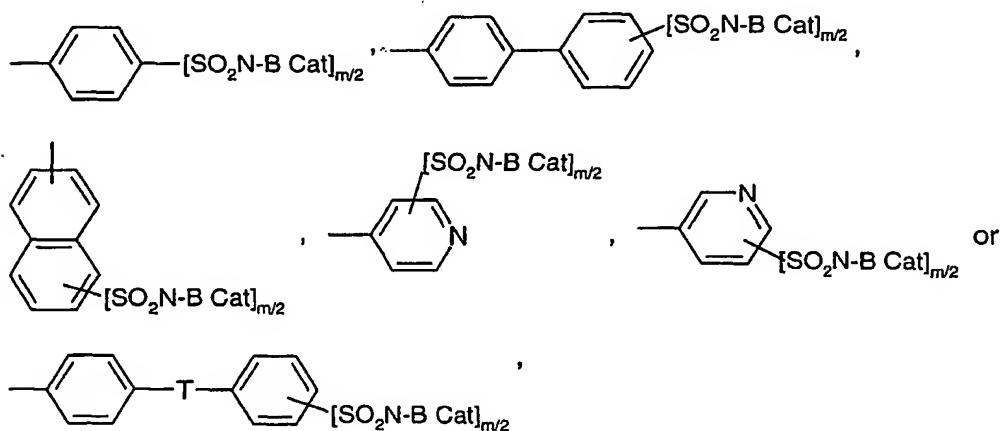


wherein R<sup>11</sup> and R<sup>12</sup> are each independently of the other hydrogen, halogen, C<sub>1</sub>-C<sub>24</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>alkoxy or phenyl and m denotes a value from 1 to 4, especially from 2 to 3;

10 - a pyrrolo[3,4-c]pyrrole derivative of formula

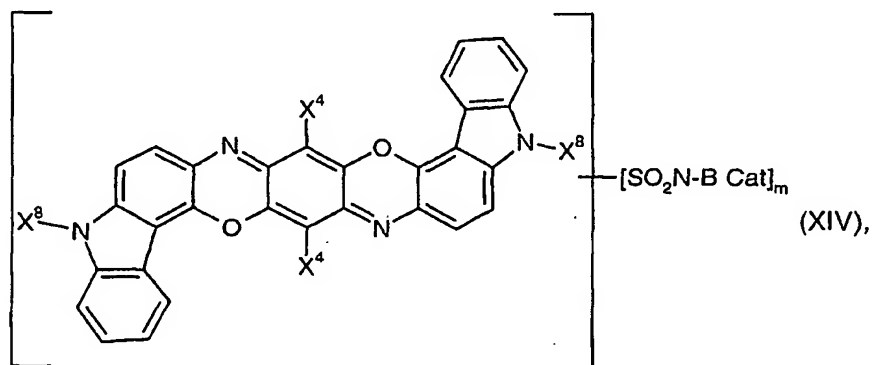


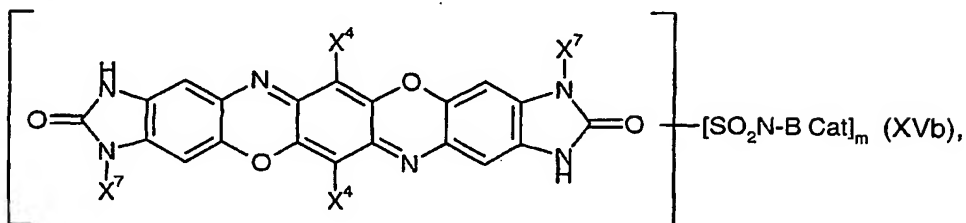
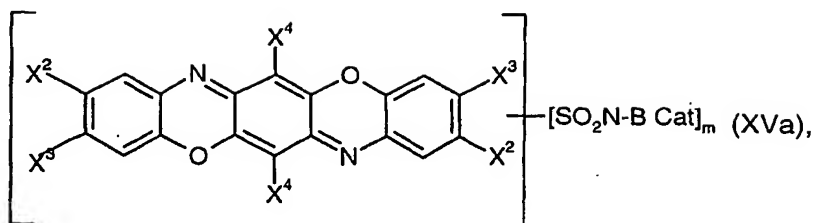
wherein Ar<sup>1</sup> and Ar<sup>2</sup> are each independently of the other a group of formula



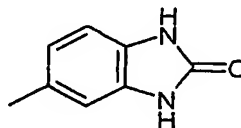
wherein T is -CH<sub>2</sub>-, -CH(CH<sub>3</sub>)-, -C(CH<sub>3</sub>)<sub>2</sub>-, -CH=N-, -N=N-, -O-, -S-, -SO-, -SO<sub>2</sub>- or -NR<sup>13</sup>-, wherein R<sup>13</sup> is hydrogen or C<sub>1-6</sub>alkyl, especially methyl or ethyl, and m denotes a value from 1 to 4, especially from 2 to 3;

- a dioxazine derivative of formula



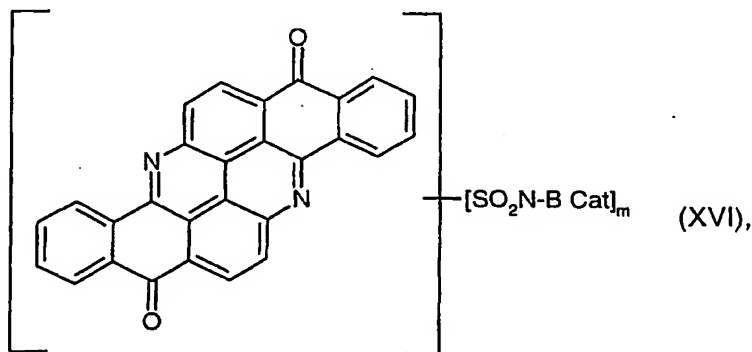


wherein  $X^2$  is a  $C_{1-4}$ alkoxy radical, especially ethoxy,  $X^3$  is a  $C_{1-4}$ acylamino group, especially an acetylamino group, or a benzoylamino group and  $X^4$  is a chlorine atom or a radical  $NHC(O)CH_3$ ,  $X^7$  is a hydrogen atom, a  $C_{1-8}$ alkyl radical, a substituted or unsubstituted phenyl, benzyl, benzanilide or naphthyl group, a  $C_{5-7}$ -

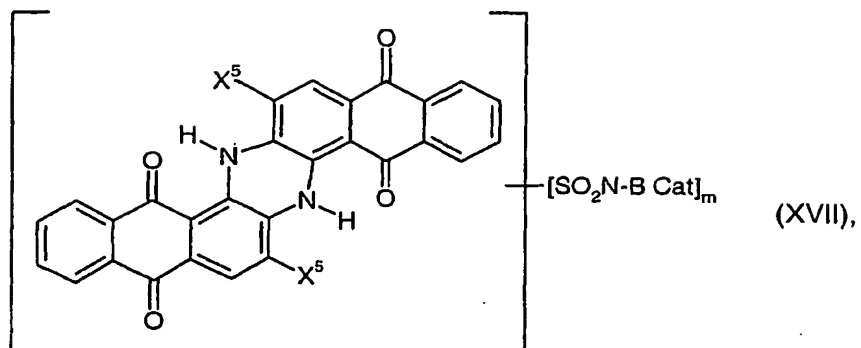


cycloalkyl radical or a radical of formula  $X^8$  is a hydrogen atom or a  $C_{1-4}$ alkyl radical and m denotes a value of from 1 to 4;

- a flavanthrone derivative of formula

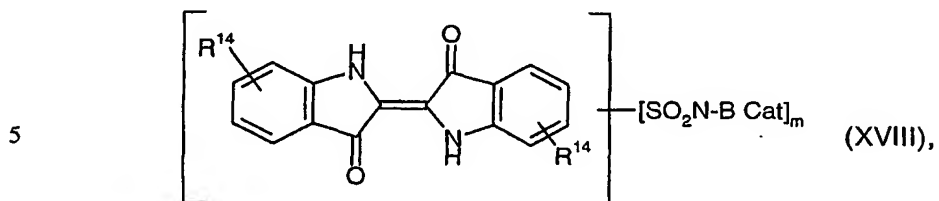


wherein m denotes a value from 1 to 4, especially from 2 to 3;  
- an indanthrone derivative of formula



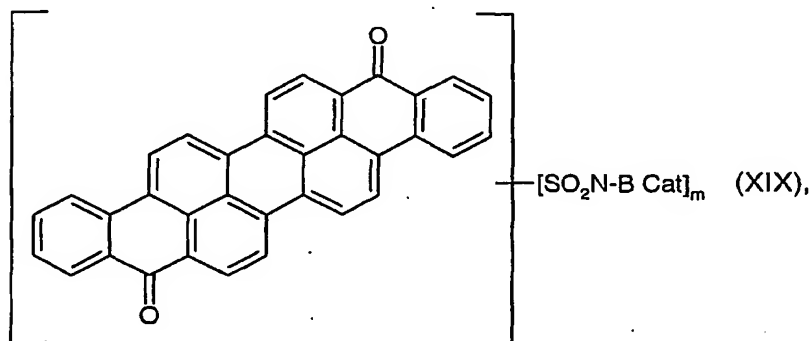
wherein  $X^5$  is a hydrogen or chlorine atom and  $m$  denotes a value from 1 to 4, preferably from 2 to 3;

- an indigo derivative of formula



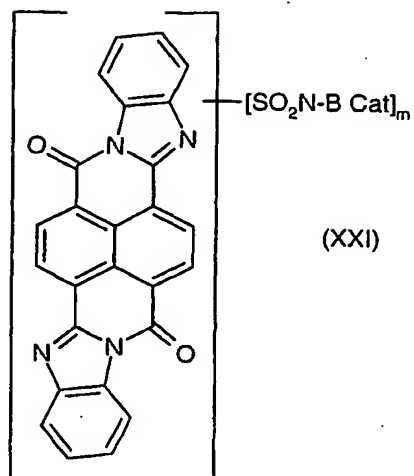
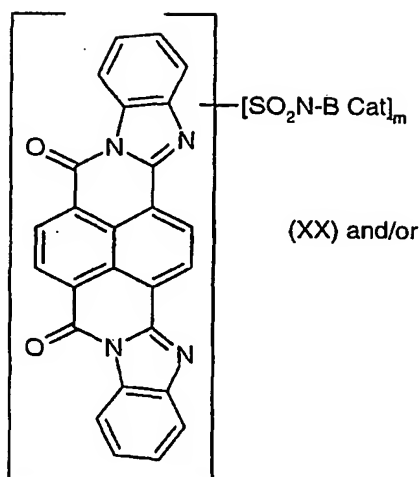
wherein  $R^{14}$  is hydrogen, CN,  $C_{1-6}$ alkyl,  $C_{1-6}$ alkoxy or halogen and  $m$  denotes a value from 1 to 3;

- an isoviolanthrone derivative of formula:



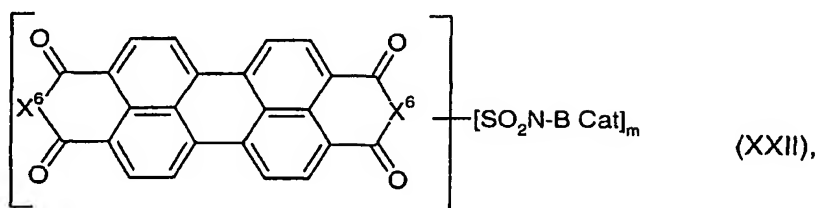
10 wherein  $m$  denotes a value from 1 to 4,

- a perinone derivative of formula



wherein m denotes a value from 1 to 4;

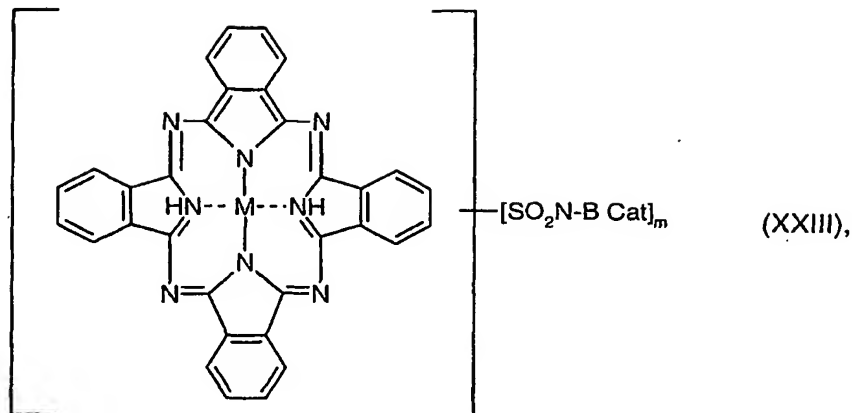
- a perylene derivative of formula



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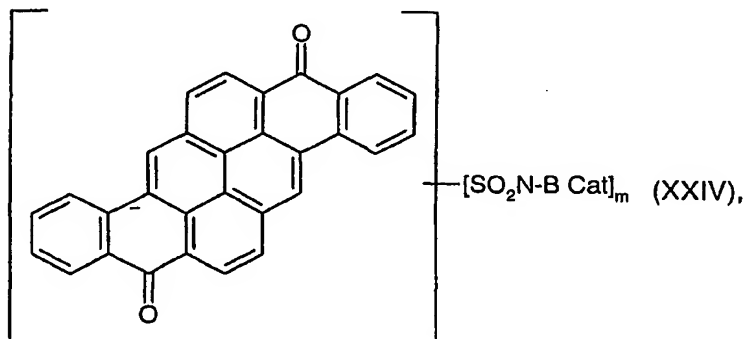
in which  $X^6$  is O or  $NR^{15}$ ,  $R^{15}$  being H,  $CH_3$  or unsubstituted or substituted phenyl or  $C_{7-11}$ alkyl, such as benzyl or 2-phenylethyl, and m denotes a value from 1 to 4, especially from 2 to 3, it being possible for the phenyl ring to be substituted by methyl, methoxy, ethoxy or by  $-N=N-Ph$ ;

- a phthalocyanine derivative of formula



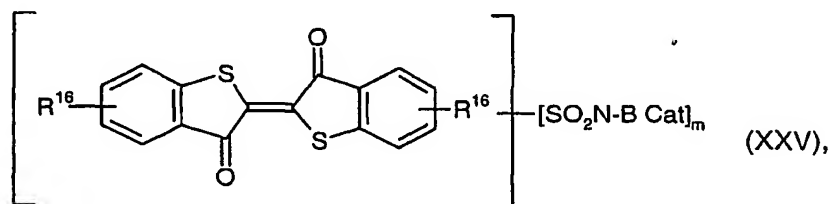
wherein M is H<sub>2</sub>, a bivalent metal selected from the group Cu(II), Zn(II), Fe(II), Ni(II), Ru(II), Rh(II), Pd(II), Pt(II), Mn(II), Mg(II), Be(II), Ca(II), Ba(II), Cd(II), Hg(II), Sn(II), Co(II) and Pb(II), or a bivalent oxo metal selected from the group V(O), Mn(O) and TiO, and m denotes a value from 2 to 6, especially from 3 to 5;

- a pyranthrone derivative of formula



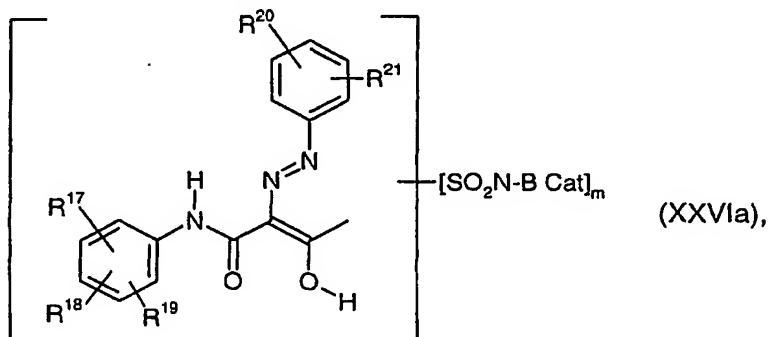
or a bromo-, chloro- or bromo- and chloro-halogenated derivative of the basic structure, for example the 2,10-dichloro, 4,6- or 6,14-dibromo derivative, wherein m denotes a value from 2 to 4,

- a thioindigo derivative of formula

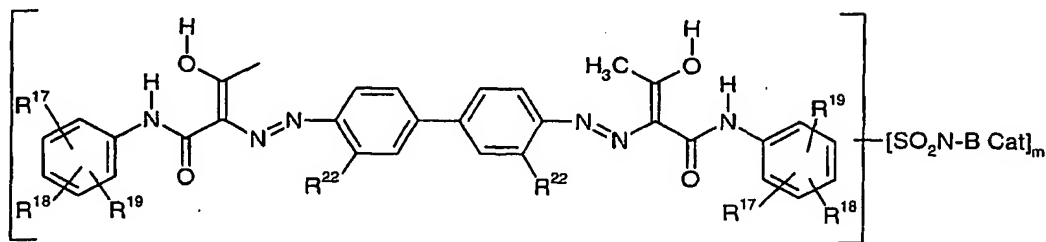




wherein  $R^{16}$  is hydrogen, CN,  $C_{1-6}$ alkyl, especially methyl,  $C_{1-6}$ alkoxy, especially methoxy, or halogen, especially chlorine, and m denotes a value from 1 to 3,  
 - a monoazo yellow and orange derivative of formula

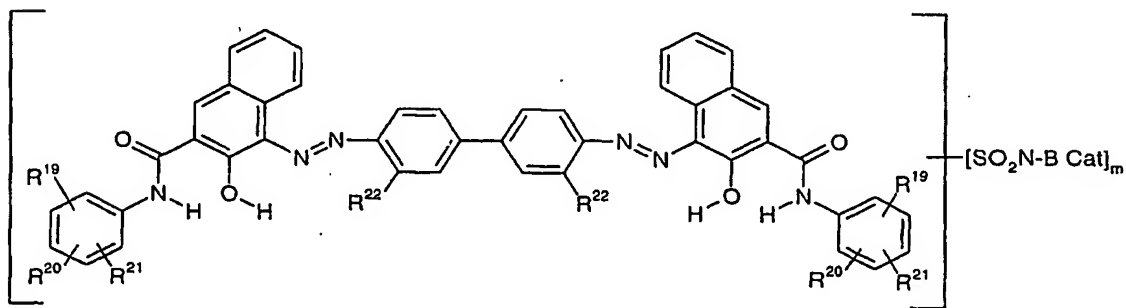


5 wherein m denotes a value from 1 to 4,  
 - a diaryl yellow pigment derivative of formula



(XXVIb), wherein m denotes a value from 2 to 4,  
 - a naphthol AS pigment derivative of formula

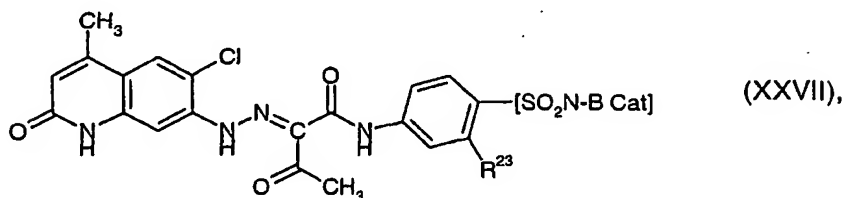
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(XXVIc), wherein m denotes a value from 2 to 6,

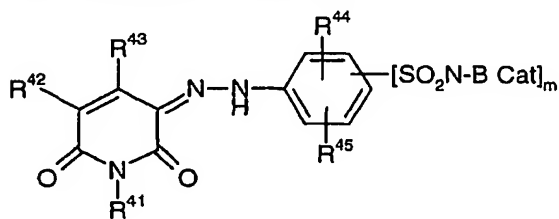
$R^{17}$  to  $R^{21}$  are each independently of the others a hydrogen atom, a halogen atom,  $C_{1-6}$ alkyl,  $C_{1-6}$ alkoxy, a nitro group or an acetyl group and  $R^{22}$  is a hydrogen atom, a halogen atom,  $C_{1-6}$ alkyl or  $C_{1-6}$ alkoxy,  
 - a monoazoquinolone pigment of formula

5



wherein  $R^{23}$  is hydrogen, halogen,  $C_{1-4}$ alkyl,  $C_{1-4}$ alkoxycarbonyl,  $C_{1-4}$ alkylcarbonyl or  $C_{1-4}$ alkanoylamino, and  
 - an azo pigment of formula

10



15

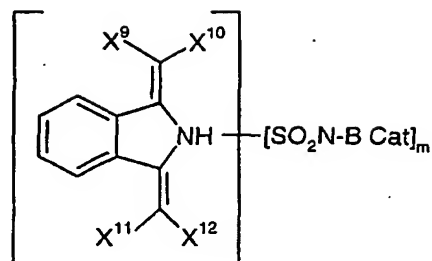
$R^{41}$  is a hydrogen atom, a  $C_{1-4}$ alkyl radical, such as methyl or ethyl, or a perfluoro- $C_{1-4}$ alkyl radical, such as trifluoromethyl, a hydroxy- $C_{1-4}$ alkyl radical or a  $C_{1-8}$ alkyl radical interrupted one or more times by -O-, such as  $CH_2CH_2CH_2-O-CH(CH_3)_2$ , a  $C_{6-12}$ aryl radical, such as phenyl, or a  $C_{7-12}$ aralkyl radical, such as benzyl,  
 $R^{42}$  is a hydrogen atom, or a cyano or carbonamide group,  
 $R^{43}$  is a hydrogen atom, a carboxylic acid group or a salt thereof or a  $C_{1-4}$ alkyl radical,

20

$R^{44}$  and  $R^{45}$  denote a  $C_{1-4}$ alkyl radical, such as methyl or ethyl, a perfluoro- $C_{1-4}$ alkyl radical, such as trifluoromethyl, a  $C_{1-4}$ alkoxy radical, such as methoxy or ethoxy, a nitro group, a halogen atom, such as chlorine,  $COOR^{46}$ , wherein  $R^{46}$  is a  $C_{1-4}$ alkyl radical, a  $C_{6-12}$ alkyl radical that is unsubstituted or substituted, for example, by one or two chlorine atoms, such as phenyl or 1,4-dichlorophenyl, or a  $C_{7-11}$ aralkyl radical, such as benzyl,  $CONHR^{47}$ , wherein  $R^{47}$  is a  $C_{1-4}$ alkyl radical, a  $C_{6-12}$ aryl radical, such as phenyl, or a  $C_{7-11}$ aralkyl radical, such as benzyl, and m denotes a value from 1 to 2,

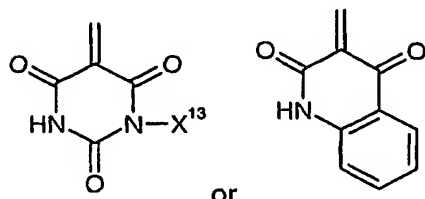
25

- an isoindoline pigment of formula



(XXIX), wherein

$X^9$ ,  $X^{10}$ ,  $X^{11}$  and  $X^{12}$  are CN, CONH-C<sub>1-8</sub>alkyl or CONH-C<sub>6-12</sub>aryl or  $X^9$  and  $X^{10}$  and/or  $X^{11}$  and  $X^{12}$  are each members of a heterocyclic ring, such as

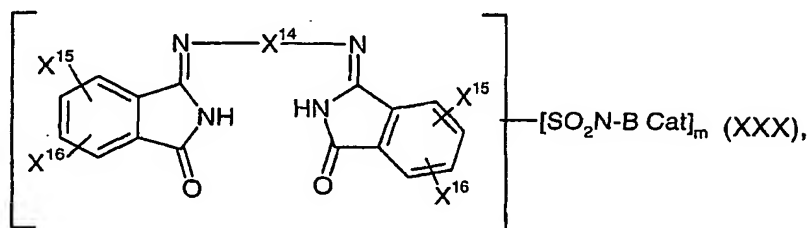


or

, wherein  $X^{13}$  is a hydrogen atom or a C<sub>6-12</sub>aryl

radical, and m denotes a value from 1 to 4,

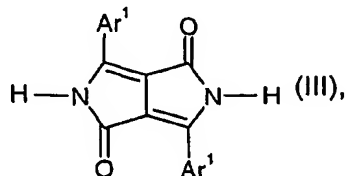
- an isoindoline pigment of formula



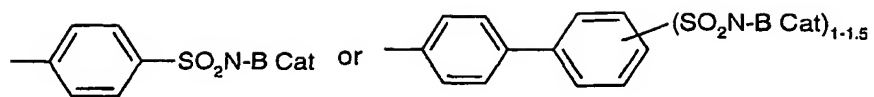
wherein  $X^{14}$  is the radical of an aromatic or heteroaromatic diamine and  $X^{15}$  and  $X^{16}$  are a hydrogen atom, a C<sub>1-4</sub>alkyl radical, a C<sub>1-4</sub>alkoxy radical, a nitro group or a chlorine atom and m denotes a value from 1 to 3, and

B and Cat are as defined in claim 1.

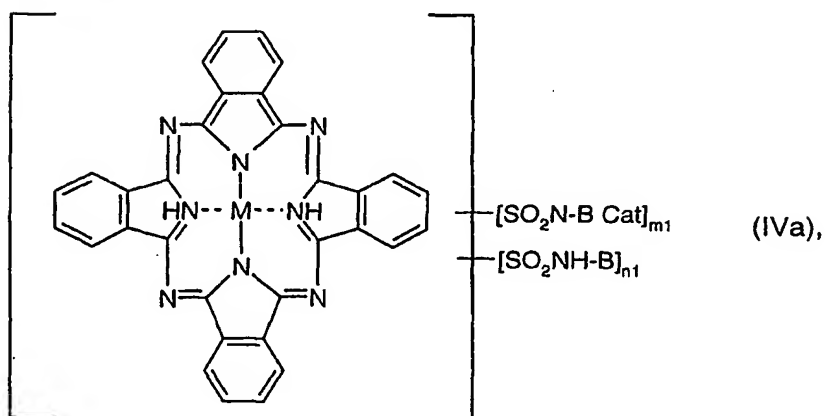
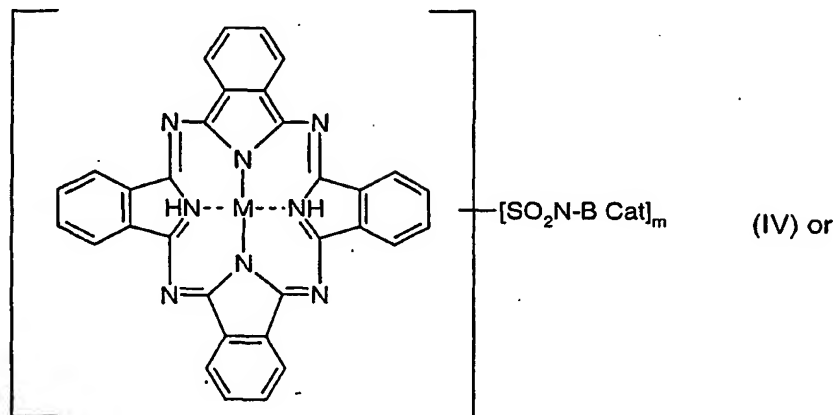
5. A colorant according to claim 4, namely a pyrrolo[3,4-c]pyrrole derivative of formula



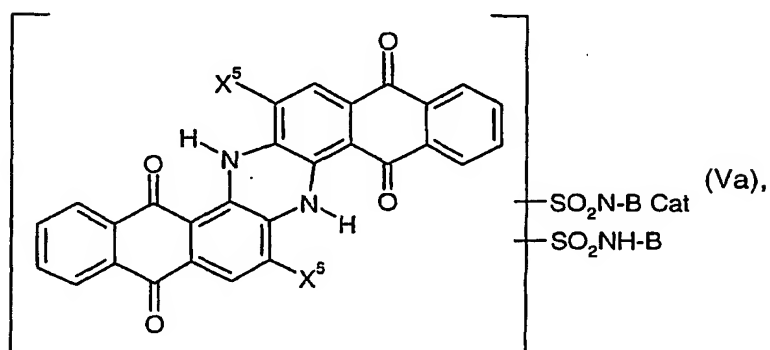
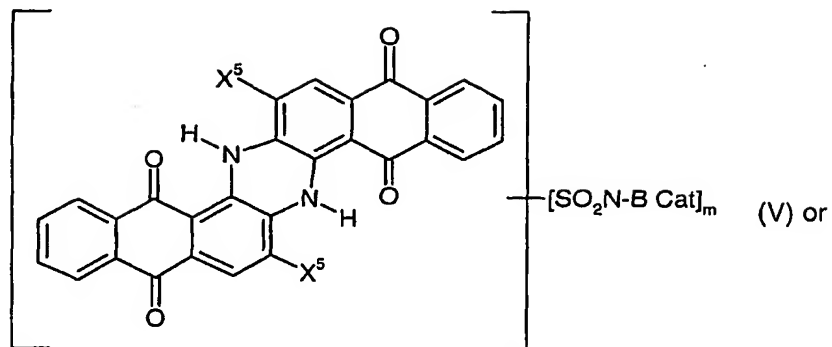
wherein  $Ar^1$  is a group of formula



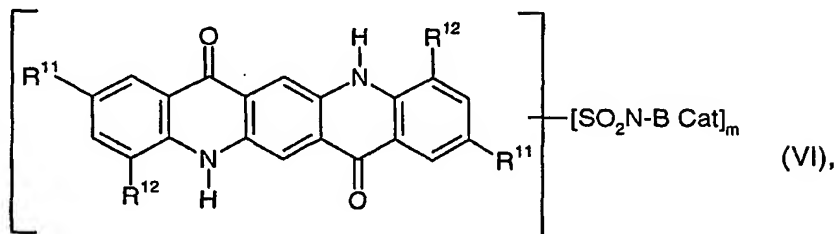
a phthalocyanine of formula



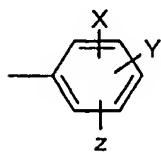
- 5 wherein M is Cu(II) or Zn(II) and m denotes a value from 3 to 5, m1 and n1 denote a value from 1 to 4, especially 1 to 3, wherein the sum of m1 and n1 being 3 to 5, especially 4,  
an indanthrone of formula



wherein  $X^5$  is a hydrogen or chlorine atom and  $m$  denotes a value from 2 to 4, or a quinacridone pigment of formula

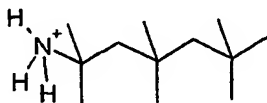


wherein  $R^{11}$  and  $R^{12}$  are each independently of the other hydrogen, a chlorine atom or a methyl group,  $m$  denotes a value from 1 to 4, and  $B$  is a group  $-(CH_2)_e-E$  or



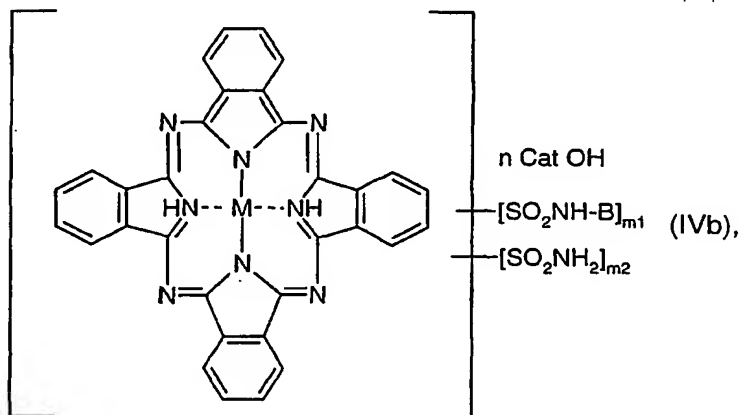
, wherein  $e$  is an integer from 1 to 6, especially 2 or 3,  $E$  is a hydrogen atom or a group  $-OH$ ,  $-OCat$ ,  $-SH$ ,  $-SCat$ ,  $-OR^1$ ,  $-SR^2$ ,  $-NR^5R^6$  or  $-C(O)OR^3$ , and  $X$ ,  $Y$  and  $Z$  are each independently of the others selected from a hydrogen atom and a group  $-OH$ ,  $-OCat$ ,  $-SH$ ,  $-SCat$ ,  $-OR^1$ ,  $-SR^2$ ,  $-NR^5R^6$  and  $-C(O)OR^3$ ,

wherein  $R^1$ ,  $R^2$  and  $R^3$  are each independently of the others a  $C_{1-4}$ alkyl radical, especially methyl or ethyl, and  $R^5$  and  $R^6$  denote a radical  $-(CH_2)_oOH$ , wherein  $o$  is an integer from 2 to 6, especially 2 or 3, and Cat is a sodium or potassium cation or unsubstituted ammonium or an ammonium cation, such as tetramethylammonium,

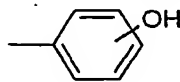


tetraethylammonium or , mono-, di- or tri-ethanolammonium or mono-, di- or tri-isopropanolammonium, N-methyl-N-ethanolammonium or 2-, 3- or 4-hydroxyphenylammonium.

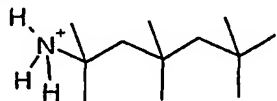
6. A colorant according to claim 1, namely



wherein M is Cu(II) or Zn(II),  $m_1$  denotes a value from 0 to 3,  $m_2$  denotes a value from 1 to 8, the sum of  $m_1$  and  $m_2$  being 3 to 5, especially 4,  $n$  denotes a value

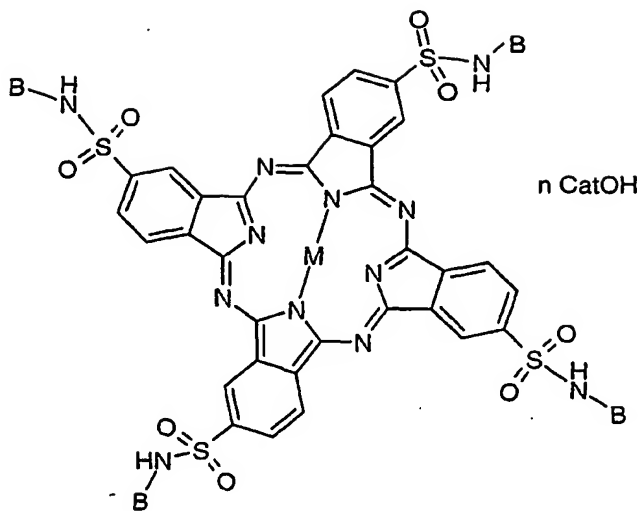


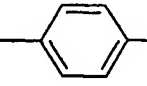
from 1 to 8, B is a group  $-(CH_2)_e-E$  or , wherein  $e$  is an integer 2 or 3, E is a hydrogen atom, a group -OH, -SH, -OR<sup>1</sup>, -SR<sup>2</sup>, -NR<sup>5</sup>R<sup>6</sup> or -C(O)OR<sup>3</sup>, and Cat is a sodium or potassium cation or unsubstituted ammonium or an ammonium cation, such as tetramethylammonium, tetraethylammonium



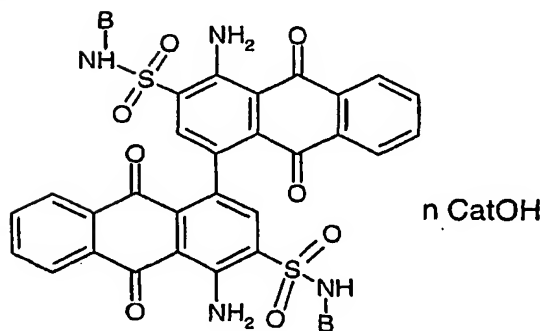
or , mono-, di- or tri-ethanolammonium or mono-, di- or tri-isopropanolammonium, N-methyl-N-ethanolammonium or 2-, 3- or 4-hydroxyphenylammonium, especially

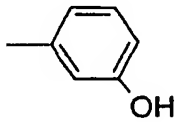
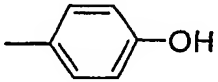
- 62 -



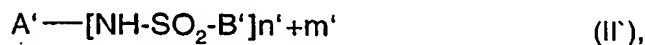
B	M	n Cat
$-(CH_2)_2-OH$	Cu	4 $Li^+$
3 H / 1  -OH	Cu	3 $Na^+$
"	Cu	7 $Na^+$
H	Cu	2 $Na^+$
$-(CH_2)_2OH$	Cu	8 $NH_4^+$
H	Cu	1 $Na^+$
2 $-(CH_2)_2OH$ / 2 H	Cu	1 $Na^+$

or



B	n Cat
	2 Na <sup>+</sup>
"	1 Na <sup>+</sup>
"	3 Na <sup>+</sup>
-(CH <sub>2</sub> ) <sub>2</sub> -OH	1 Na <sup>+</sup>
-(CH <sub>2</sub> ) <sub>2</sub> -OH	2 Na <sup>+</sup>
H	1 Na <sup>+</sup>
H	2 Na <sup>+</sup>
	2 Na <sup>+</sup>

7. Use of a colorant of general formula I or II according to any one of claims 1 to 6,  
for the pigmenting of porous materials, especially for the pigmenting of wood or  
anodised aluminium in the pores, and in inkjet printing.
8. Method of pigmenting a porous material, especially for the pigmenting of wood or  
anodised aluminium in the pores, comprising
- a) treatment of the substrate with an aqueous solution of the colorant of general  
formula I or II according to any one of claims 1 to 6, and
- b) conversion of the colorant to a pigment of formula I' or II'



wherein A and A', B and B', m and m' and n and n' are as defined in claim 1.

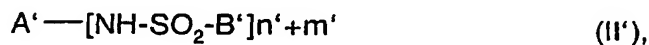
9. A porous material obtainable according to the method according to claim 8.



10. A porous material comprising pigments of general formula I' or II'



or

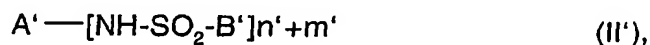


wherein A, B and B', m and m' and n and n' are as defined in claim 1.

11. A coloured aluminium pigment that comprises platelet-shaped aluminium substrates coated with a metal oxide layer, the metal oxide layer comprising pigments of the general formula I' or II'



or



wherein A, B and B', m and m' and n and n' are as defined in claim 1, and the metals of the metal layer are selected from vanadium, titanium, zirconium, silicon, aluminium and boron.

Internal Application No  
PCI/EP 02/04071

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C09B69/02 C09B69/00 C09B67/44 C09B67/00 C09D11/00

#### B. FIELDS SEARCHED

IPC 7 C09B

EPO-Internal, WPI Data, PAJ

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☒ Patent family members are listed in annex.

\*& document member of the same patent family

21/08/2002

Dauksch, H

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